VOLUMETRIC ANALYSIS

COBLENTZ AND VORISEK

A MANUAL

OF

VOLUMETRIC ANALYSIS

TREATING ON THE SUBJECTS OF

INDICATORS, TEST-PAPERS, ALKALIMETRY, INCLUDING ASSAY OF DRUGS
BY TITRATION, ACIDIMETRY, ANALYSIS BY OXIDATION AND
REDUCTION, IODOMETRY, DETERMINATIONS BY PRE-
CIPITATION, AND BY COLOR COMPARISON

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SECOND EDITION
REVISED, COMPLETELY RECONSTRUCTED AND ENLARGED

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With 37 Illustrations

PREFACE TO SECOND EDITION.

The revision of the volume was undertaken with the view of enlarging its scope and adapting it still more to the laboratory and class-room needs. That, in the reconstruction, radical changes were made is chiefly due to the objects aimed at, though no less, to the complete freedom enjoyed in carrying out the plan of the work.

The principles underlying a determination are given in brief and the description of the operation is made as concise as possible.

The method of derivation of factors (equivalents of unit volume of volumetric solutions) from equations is given in all typical cases and the calculation of results illustrated by examples or indicated by formulæ.

Comments, or other explanatory informations thought necessary, are given as observations or notes on the operations. It is recommended that these be perused before any particular determination is first undertaken.

While the introduction of many multiple methods had to be avoided, more than one method will be found included for certain substances. This was deemed advisable in order to furnish exercises for the student in checking results and of comparing the merits of different methods.

Direct percentage estimations, differing from other determinations only in the manner of calculation of the results, are no longer treated under a separate heading.

The discussion of ionic state of electrolytes in solution has been extended to chemical reactions other than those of the indicators on the assumption that the teacher and the student using the volume are acquainted with the fundamental physical laws underlying analytical chemistry; for those to whom this will come as an innovation, it is sincerely hoped, such extension may serve as an incentive to turn some of their attention to physical chemistry.

As the standard temperature that of 20° C. is recommended for adoption; however, the actual selection is left to the judgment of the analyst.

The atomic weights employed are those published for 1909 by the International Committee on Atomic Weights, the basis of which is oxygen $= 16$. Attention is directed to the use, in this volume, of $H = 1.01$ instead of the official 1.008. This rounded value, adopted by many, is used to shorten long fractions and to facilitate calculations.

<div align="right">A. V.</div>

New York, June, 1909.

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PREFACE TO FIRST EDITION.

This manual is intended to serve as a systematic introduction to the principles of volumetric analysis based on modern theories. Especial attention has been devoted to the theory of ionization and its application to indicators, also the necessary precautions as to dilution, temperature, and influence of disturbing elements—factors frequently overlooked in volumetric analysis.

As a guide for the selection of a proper indicator, the detailed descriptions are followed by a table which should be consulted by the beginner before carrying out a saturation titration.

The most important factor in volumetric analysis is the preparation and accurate standardization of the reagent solutions; in view of this, several different methods of standardization, with practical examples, are given in each case in order that the operator may learn to properly check his work.

Each different titration method is illustrated by one or more practical exercises which serve as aid to the student in the calculation of the various problems which present themselves.

In order to avoid possible confusion to the beginner direct percentage estimations are treated under a separate heading after the general principles have been thoroughly considered.

The readiness with which many standard solutions lose their titer on standing, the loss of time entailed in re-standardizing, also the convenience with which these empirical solutions may be prepared and utilized in titrating, led the author to devote a special section to this subject, which is continued throughout the text in the form of practical examples.

Under the titrimetric methods of alkaloid estimation, it has been the endeavor to impress upon the operator the necessity of accurately observing such important conditions as the careful selection and application of indicators, the nature and volume of the solvent, the precautions necessary in handling the very dilute standard solutions, etc., for unless all these are fully complied with no reliance can be placed upon results.

The didactic system ($H = 1.000$) of atomic weights has been adopted on the consideration that it is the oldest, most familiar and comprehensive to the student of chemistry.

New York City.

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VOLUMETRIC ANALYSIS.

CHAPTER I.

INTRODUCTORY.

Chemical Analysis, when it is concerned with the detection, separation and identification of the constituents of any definite chemical compound or the ingredients of a heterogeneous mixture, is known as *qualitative* chemical analysis. If, in addition, the quantity of the components present is determined, *quantitative* chemical analysis is performed. Since the presence of any such constituent to be determined must be known before the determination of the amount of it present can be undertaken, qualitative must precede quantitative analysis.

Depending on the method of measuring, quantitative analysis is mainly divided into:

Gravimetric analysis,
Volumetric analysis.

In *gravimetric* analysis the constituent to be determined is separated by itself or in some definite chemical combination of known composition and the weight of the isolated body is ascertained. Generally a small quantity of the sample is accurately weighed and dissolved. An excess of a reagent which precipitates the component desired is then added and the precipitate, after purification and drying, is carefully weighed. The product obtained being pure and of definite composition, the quantity of the constituent sought which is present in it is readily obtained from its weight by calculation. It is to be well noted that in the gravimetric method of determination the exact weight of the product of a reaction serves as a basis for calculation of the results, no attention being paid to the actual quantity of the reagent or the strength of its solution, employed to produce it. In fact the exact amount of the reagent need not be known; addition of the reagent being almost always continued until an excess is present.

In *volumetric* analysis the calculation of results is based on the actual quantity of a reagent required to completely react with the substance to be determined, no attempt being made to measure the amount of the product. In actual operation a small quantity of the sample is accurately weighed and dissolved. Solution of the proper reagent, whose exact strength at the time of the determination must be known, is then carefully added from a measuring vessel until the reaction that takes place is completed. From the volume of the solution of the reagent consumed by the sample, the quantity

quantity will be somewhat changed and will then be the exact equivalent of 8 Gm. of oxygen. The ratio of these two elements according to the 1909 table of atomic weights is $H:O::1:15.87$, while $O:H::16:1.008$, and therefore their equivalents are 2.016 of $H = 16$ of O.

The equivalent quantity of any reagent which corresponds to the unit of valence is in the case of acids dependent on their basicity, in bases, on their acidity and in the neutral salts on the number and the valence of the reacting atoms of an element which alone, or as constituent of a compound, takes active part in any particular chemical reaction. Thus, for example, Normal V. Solutions of the following reagents contain in 1000 Cc.: HCl, M.W. $= 36.47$, contains 36.47 Gm.; H_2SO_4, M.W. $= 98.09$, contains 49.045 Gm. the acid being dibasic; NaOH, M.W. $= 40.01$, contains full amount 40.01 Gm.; $Ba(OH)_2$, M.W. $= 171.39$, contains 85.695 Gms. being a diacid base; $AgNO_3$, M.W. $= 169.89$, contains 169.89 Gm. the reactive Ag being monovalent; but potassium dichromate, M.W. $= 294.4$ contains, when used as an acid salt, 147.2 Gm. being dibasic, and 49.066 Gm. only, when used as an oxidizing agent, the molecule containing 3 active atoms of oxygen. In the same way potassium permanganate, M.W. $= 316.06$ contains 3.1606 Gm. in 1000 Cc. of $\frac{N}{10}$ V.S. because its molecule contains 5 active oxygen atoms.

Fraction-Normal V.S. bear a simple relation to normal solutions and are mostly prepared from these by proper dilution. Sometimes, solutions stronger than normal are also used and these are made twice or other number times stronger than the normal. Therefore:

Normal V.S. (N) contain in 1 Lt. a quantity of reagent equivalent of 8 Gm. of oxygen. Half-normal V.S. ($\frac{N}{2}$) contain $\frac{1}{2}$ of the quantity equivalent of 8 Gm. of oxygen. Fifth-normal V.S. ($\frac{N}{5}$) contain $\frac{1}{5}$ of the quantity equivalent of 8 Gm. of oxygen. Tenth-normal V.S. ($\frac{N}{10}$) contains $\frac{1}{10}$ of the quantity equivalent of 8 Gm. of oxygen. Hundredth-normal V.S. ($\frac{N}{100}$) contain $\frac{1}{100}$ of the quantity equivalent of 8 Gm. of oxygen. Double-normal V.S. (2N) contain $2 \times$ the quantity equivalent of 8 Gm. of oxygen in 1000 c.c.

Similarly are constituted solutions of other normal strengths.

The adoption of this system of strength relations placed V.S. on an equivalent basis and their application became greatly extended. The quantity of a reagent in any volume of a solution of normal or fraction-normal strength is readily derivable and any volume of such solution must exactly correspond to an equal volume of any other solution of the same normal denomination.

Volumetric solutions of any known strength may be changed to solutions of normal strength. Let a standard solution be stronger than the nearest N-V.S.; then, by proper dilution, its strength may be reduced to normal; while, if the solution is weaker than the nearest normal V.S., a stronger standard solution of the same reagent may be added to it in such proportion as to bring its strength to the desired value, or, the reagent itself may be added. In that case—it being impracticable to adjust the strength directly— the reagent is added in amount sufficient to produce a stronger than desired solution and when the exact strength of this has been found,

diluting with the required volume of water. It is always necessary, however, after such adjustments have been made, to confirm or check the strength of the solution. This is accomplished with the aid of another exact solution of normal strength or with a definite quantity of a pure reagent with which the one in solution reacts.

Since all V.S. change their strength more or less on keeping, adjustment to the normal strength, at best rather difficult, involves a considerable loss of time.

Empirical V.S. are standard solutions of other than the normal strength. Normal V.S. when through any cause changed in value, become empirical V.S. Empirical V.S. are, therefore, the more common and are not as a rule converted into the nearest normal. Their exact strength when determined, is expressed in two ways: either as per cent. of the nearest normal V.S., or, the exact quantity of the reagent present contained in unit volume of the solution is indicated. If, for example, 30 Cc. of normal alkali were found to require, for complete neutralization, 32 Cc. of an acid, then the acid is weaker than normal and its value in per cent. of the N-V.S. is found by proportion:

$$32 : 30 :: 100 : x = 93.75 \text{ per cent.}$$

This shows that 1 Cc. of the empirical acid corresponds to 0.9375 Cc. of N alkali, or, equals as much of its own N-V.S. Therefore, when empirical V.S. are used in analysis, the number of cubic centimeters of any such solution consumed, multiplied by its percentage strength, give the volume of the nearest N-V.S. they equal. Since the quantity of a reagent in its normal V.S. is always known, it is not difficult to calculate the quantity of the absolute reagent in a unit volume of the empirical V.S. If, then, the acid under consideration happened to be HCl, of which by definition, 1 Cc. of N-V.S. contains 0.03647 Gm., then 0.03647 × 0.9375 will give the quantity desired.

Standard Temperature.—To be accurate, all V.S. must be prepared at some adapted temperature called standard temperature, and should not be used without correction of their volumes if their temperature, at the time of determination, varies more than two to three degrees, either way, from the standard adopted. This standard of temperature is entirely arbitrary, though in selecting it, such temperature should be chosen which most nearly represents the average working conditions of a laboratory during the year.

The U.S.P. standard temperature, 25° C., is regarded by many to be somewhat high and though easily attained is not always conveniently maintained, while that of 15° C. previously used and still recognized by other authorities is justly criticized as low. The lower temperature is found unsuited for exact measurements especially in calibrating measuring vessels. When a vessel, filled with a liquid at 15° C., is to be weighed in a room the temperature of which is higher than 15° C., moisture will readily deposit on the outside of the vessel, making accurate weighing almost impossible. Nor is the lower temperature easily maintained on warmer days.

For these reasons and objections a temperature near the average of these two extremes is finding favor and wide application. Temperature of 20° C. will then be found most valuable, though 18° C. and also 17.5° C. are adopted by some.

Correction for Temperature.—Correction of the volume of V.S. for temperature is necessary only when titrations have been made at temperatures outside of the limits specified, or when comparison of results is to be made with determinations carried out at some other standard temperature. Ordinarily, therefore, no correction is necessary. But as all liquids do not expand or contract equally for the same deviation in temperature, there being no general law of liquid expansion, different corrections, obtained experimentally, must be applied for each particular liquid. Some reagents, chiefly the salts, when dissolved in water, lower the temperature of the solvent, while others, such as the acids, increase it under similar conditions. The temperature of a solution should, therefore, be properly ascertained and brought to the standard before the solution is measured.

The rate of expansion is different for different reagents in solution and varies also with the strength of the solution of the same reagent. In the case of water the rate is variable for the same number of degrees at different temperatures. To correct a volume of any solution for temperature, the rate of expansion of the solution must be known. The following table gives the results of some experimental determinations:

TABLE SHOWING EXPANSION OF 1000 CC. OF A LIQUID FOR 10° C. (WARMED FROM 15° TO 25°). A. SCHULZ.

	Cc.
Water	2.05
$\frac{N}{10}$ NaCl	2.06
$\frac{N}{10}$ $K_2Mn_2O_8$	2.13
$\frac{N}{10}$ $AgNO_3$	2.16
N HCl	2.42
N $H_2C_2O_4$	2.62
N Na_2CO_3	3.03
N H_2SO_4	3.05
N HNO_3	3.07
N NaOH	3.15

Corrections can not be satisfactorily applied to strong solutions of the alkalies. In the case of the $\frac{N}{10}$ V.S. corrections may be readily made by employing factors such as are given in the following table:

TABLE OF FACTORS FOR CORRECTION OF $\frac{N}{10}$ V.S. FOR TEMPERATURE BASED ON NORMAL TEMPERATURE OF 20° C.

Temperature. °C.	Correction Factor.	Temperature. °C.	Correction Factor.
5	1.00180	10	1.00146
6	1.00178	11	1.00136
7	1.00175	12	1.00125
8	1.00160	13	1.00113
9	1.00154	14	1.00100

Tempera- ture. °C.	Correction Factor.	Tempera- ture. °C.	Correction Factor.
15	1.00096	21	0.99980
16	1.00081	22	0.99959
17	1.00065	23	0.99937
18	1.00038	24	0.99914
19	1.00020	25	0.99890
20	1.00000		

The number of Cc. of a V.S. used in titration multiplied by the factor corresponding to the temperature at which the solution is measured, gives the volume of the V.S. at 20° C. If, for example, 50 Cc. of a $\frac{N}{10}$ V.S. at 10° C., were used at normal temperature, their volume would be:

$$50 \times 1.00146 = 50.023 \text{ Cc.}$$

Preparation and Keeping of Volumetric Solutions.

The reagents used for V.S. must be of high degree of purity and distilled water should invariably be employed for the aqueous solutions. When standardized, V.S. are to be placed in clean bottles which, if not dry, are first rinsed with distilled water and then with several portions of the solution before filling. Bottles should be provided with well fitting stoppers, preferably of glass, except for solutions of the alkalies for which rubber stoppers are to be employed. Solutions of the alkalies have a tendency of becoming ropy if kept in closed bottles and not in contact with air; on this account air, free from CO_2 and moisture, is allowed to enter the containers in which the solutions are kept by providing the stopper with a tube containing soda-lime (Fig. 25). The strength of V.S. should be redetermined at regular intervals which will vary with the solutions themselves, the exact strength found and the date of determination being carefully recorded. Those V.S. which change readily on keeping should be standardized at the time of their employment for titrations. All V.S. should be properly labelled and stored in a cool place and out of direct sunlight. Solutions which are acted on by light, such as silver nitrate, thiosulphate and iodine, V.S., etc., should be kept in dark-colored bottles, while those which suffer change by contact with the air may be covered with a layer of liquid petrolatum. Bottles containing very strong alkalies are readily closed with a tall, lipless beaker inverted over the neck of the bottle so that its rim rests on the shoulder of the bottle where a sealed joint is made with a ring of petrolatum. If, for any reason, it is necessary to filter a standard V.S., dry filter must be used and all parts of the solution be kept well covered during filtration to protect it from dust and to prevent vaporization.

Titration.

When to a solution of a sample the V.S. is added from a graduated vessel for the purpose of determination, the solution is said to be titrated. Titration may then be defined as the actual manipulation of adding and measuring the volume of V. solutions in determinations. Titration may be simple or residual.

Simple Titration requires the use of one V.S. to measure the amount of an ingredient in the submitted sample.

In **Residual Titration**, two V.S., mutually reacting, are employed; one reacting with the ingredient to be determined is added in excess and the unconsumed reagent (in the excess of the V.S.) is determined by titration with the other V.S. Residual titration receives its name from the fact that some of the V.S. first added is left over or constitutes a residue. This titration is sometimes called "back titration." If the two V.S. employed in residual titration are of equal value, e. g., of the same normal strength, the volume of the first V.S. consumed by the sample is found by simple subtraction.
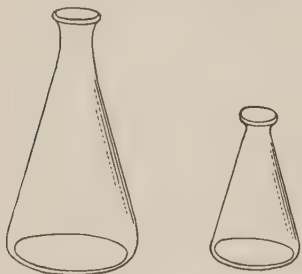
Titrations are best carried out in flasks, preferably those of the "erlenmeyer" shape as they allow proper mixing and do not upset readily. These flasks should be flat-bottomed to permit ready observation of the changes of color and should be of suitable dimensions.

FIG. 1. TITRATION FLASKS.

When a titration is performed, the tip of the measuring vessel should extend well into the neck of the flask, Fig. 2, to prevent loss; any solution adhering to the sides of the flask is to be washed into the flask when the end of the operation has been nearly reached. When the titration of the sample is to be performed in a stoppered flask or bottle, care should be exercised in opening the vessel, not to lose any of the contents.

During titrations a white background under the flask will assist detection of the changes in color. For this purpose a white porcelain plate 4×4 is admirably suited, though a sheet of white paper will answer as well. Since titration is a quantitative operation it is evident that results will be materially effected through careless manipulation and incorrect reading of the volumes of V.S. used; hence much care and attention to details must be exercised in carrying out the operation. The solutions in burettes should be protected from dust which may readily be done by covering the burette with a dry test tube containing in the bottom a small plug of absorbent cotton. To prevent absorption of CO_2 by V.S. of alkalies, the burette should be closed with a rubber stopper carrying a soda-lime tube (see Fig. 25).

Titration of Hot Solutions. — The measuring vessel from which any V.S. is delivered in titration of hot solutions should be protected from the heat radiated by such solution, otherwise vaporization of the V.S. would be greatly increased and readings could not be taken

FIG. 2. POSITION OF BURETTE IN TITRATION.

except after proper cooling. Screening the lower part of the burette is not always practicable so that it is best to place the burette in such position as not to be directly over the hot liquid. This may be accomplished by attaching a piece of glass or rubber tubing to the lower opening of the burette, in nearly horizontal position, Fig. 3, the free end of this, terminating in a glass tip, being secured above the titration flask. In any case it is advisable to find the temperature of the V.S. and read the burette only at the standard temperature adopted.

Titration by Weighing.—Titration may also be carried out by weighing the V.S. employed. For this purpose an all-glass burette, provided with a stopcock, so modified in form as to permit of its suspension from the arm of a balance, is employed; for this may be substituted a small, short stem separatory funnel. The quantity of the V.S. used in a titration, which is carried out in the usual way, is obtained as the difference of the weighings taken before and after the titration. Weighing being less rapid than measuring, more time is consumed in this operation; however, by weighing the V.S., more accurate results can be secured while the errors due to variation in temperature of the solution and imperfect draining of the burette are entirely eliminated.

The End-Reaction. — In volumetric analysis, as has already been stated, the V.S. of a reagent is added to the solution of the sample

FIG. 3. TITRATION OF HOT LIQUIDS.

until the reaction that takes place between them is completed. When one of the reacting substances has a color, the change in color which it undergoes in a reaction will indicate that the reaction is completed. Thus when the solution of potassium permanganate, which has a violet color, is added to hydrogen peroxide (colorless) in presence of sulphuric acid, the end of the reaction between them is indicated when a weak pink color is imparted to the titrated liquid. The hydrogen peroxide has then consumed all the permanganate it could react with, namely the chemical equivalent of its own weight; and the minute quantity of the permanganate which colors the solution indicates that all peroxide has been destroyed. It is true that in this instance, in fact in all titrations, the end of a reaction is indicated only when an excess of the V.S. of the reagent has been used; but in carefully performed titrations this excess will be so
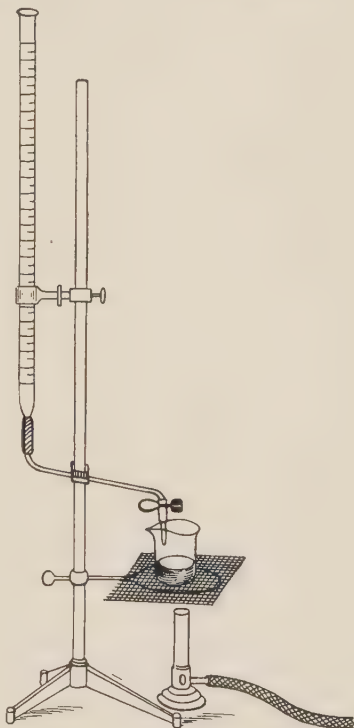
small as to be negligible. However, to overcome any error due to this cause, which in certain titration may be considerable, the titration should be, as a rule, carried out to nearly the same end-point to which the V.S. itself was standardized. With colorless or faintly colored reagents, or, in reactions involving no color changes, the end reaction can not be seen without the aid of some other agents. Thus hydrochloric acid may be mixed with a solution of sodium hydroxide in any proportion without the completion of the reaction or the excess of either being shown in any visible way. But the fact that both the acid and the alkali change certain vegetable colors when they act on them, is made use of for their detection. In titrations small quantities of one of these sensitive compounds are added for the purpose of showing the presence of an excess of the colorless reagents. The coloring matter, being affected by a minute quantity of the active reagent when in excess, serves to indicate that the reaction of one agent with another is completed. In other reactions the end-point is indicated by production of a precipitate, or when the product of a reaction is a precipitate, the end-point is indicated when such precipitate ceases to be formed.

The end of a reaction may therefore be made evident through these indications:

(*a*) Change in color of the reacting substances.

(*b*) Formation of a precipitate, or no further precipitation.

(*c*) Change in color of some other sensitive substance added for this purpose.

INDICATORS.

Indicators are sensitive substances used in titration for the purpose of showing (indicating) the completion of a reaction. Their selection depends on their sensitiveness toward the minutest excess of one or both reacting substances. They are used chiefly in solutions which should be carefully made and properly preserved away from light and dust.

Methods of Ascertaining the End-Point.—Two methods are employed. In the more common one, the indicator is added to the titrated solution at once or towards the end of the titration, the indicator reacting with one of the acting substances. In the other method which is used when the indicator reacts with both acting substances equally well, the indicator is mixed with a drop of the titrated liquid towards the end of the titration, a drop at a time being taken out and mixed with it outside the titrating vessel; hence the designation: " drop end-reaction " or, " drop end-point." With the drop end-point method a distinct reaction is obtained only when a considerable excess of the V.S. has been added, the error due to this cause increasing with the volume of the titrated solution. Further, by repeated removal of the test portions of the solution some of the sample is necessarily lost; titration in this way is, therefore, more difficult and the results are apt to be less exact. The V.S. used in these titrations are chiefly empirical and are standardized by the drop end-point method, the titrations being then carried out to the same intensity of the end-reaction color adopted in their

standardization. In this way the error caused by an excess of the reagent is effectively minimized. When titration and standardization is not made at one time, control or blank titrations should be made.

Blank Titrations.—To more accurately ascertain the end-point of a reaction in titration a solution known as blank solution is made and titrated. Such solution should be of nearly the same volume and composition, save that it does not contain the substance which is being titrated, and should be titrated, using a definite quantity of the indicator, to a distinct end-reaction. The coloration produced by one to two drops of the V.S. is usually regarded as the standard end-point. The titration of the sample is then made to nearly the same end-point. The volume of the V.S. consumed in the blank is then deducted from the volume of the same solution consumed by the sample. The importance of carrying out blank titrations of all the reagents used in the determination under as nearly identical conditions as possible, and to the same end-point to which the sample is titrated, can not be too strongly emphasized.

APPARATUS.

Results in volumetric analysis are based on the exact volumes of the V.S. used in titrations. To measure such solutions accurately, it is important that the measuring vessels employed be carefully selected and accurately calibrated at standard temperature. Again, the exact weight of the reagent in any standard V.S. must be known while the correct weight of the sample taken for titration is also required, a good analytical balance is therefore as indispensable as are exact measuring vessels.

Balance.—A short-beam, rapid weighing analytical balance of 200 Gm. capacity and of sensitiveness to 0.2 Mgm. is required. The weights, best gold or platinum plated, should be exact. Their mutual agreement should be confirmed by trial and the proper corrections applied.

Weighing.—Direct weighing is carried out in the usual way by placing the object to be weighed on one pan of the balance and adding the weights to the other pan until both are exactly counterbalanced, or, when the nature of the material permits it, adjusting the quantity of the sample by addition or removal until any desired weight of it has been secured. For weighing of most solids counterbalanced watch glasses should be used, while liquids are best weighed in small weighing bottles provided with stoppers. The use of paper in place of watch glasses for the purpose of supporting the material in weighing is to be discouraged; the weight of the paper is readily affected by atmospheric moisture, exact weighing being made impossible.

Weighing by Difference differs from direct weighing in that the quantity of the substance weighed out is obtained as the difference of two weighings. The sample is first weighed in a small, well-stoppered container, then a suitable portion is carefully poured out into a flask and the container, with the remaining substance, again weighed. By subtraction, the difference between the two quantities

is found and this constitutes the weight of the sample removed. To prevent any loss of the material removed from the weighing bottle the vessel which is to receive the portion for analysis should be .kept at hand in the weighing room. Weighing by difference is especially adapted to weighing changeable or volatile substances.

Weighing by Substitution.—To overcome errors due to imperfections in the construction of the balance, the weight of the substance is found by counterbalancing it on one pan of the balance, carefully and exactly, with some suitable material such as brass, shot or tinfoil. The substance is then removed and replaced by the necessary weights which will then represent the weight of the sample. All weighing should be carefully and accurately made and the respective weighings at once properly recorded.

Measuring Vessels.—As measuring vessels in volumetric analysis, burettes, pipettes, cylinders and flasks are employed. It is of importance that these vessels closely agree in their graduation.
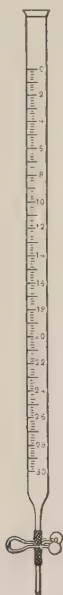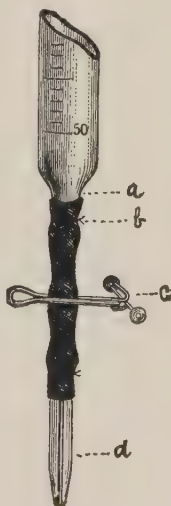

FIG. 4. MOHR BURETTE.   FIG. 5. LOWER EXTREMITY OF M.B.   FIG. 6. ALL-GLASS MOHR BURETTE.

Burettes.—Burettes are glass tubes of uniform calibre, narrowed at one end, the straight part of the tube being divided into cubic centimeters with suitable subdivisions into fifths or tenths. The Mohr burette, Fig. 4, is usually fitted with a piece of India rubber tubing to connect the discharging tip with the tapering end of the burette. The rubber tubing should be firmly fastened on with twine or thin wire, see *b*, in Fig. 5, as it is apt to slip off during titration. The flow of the liquid from this kind of burette is regulated by a pinchcock, *c*, in Fig. 5, or by means of a glass bead (section of

a glass rod) placed within the rubber tubing, while the volume of the discharge is controlled by varying the pressure applied to either. In the all-glass Mohr burette, Fig. 6, which is provided with a glass stopcock, the stopper should be regularly lubricated with a minute quantity of petrolatum or glycerin applied to its dry surface.

Burettes, with rubber attachments, should not be used for certain V.S., such as potassium permanganate, silver nitrate, iodine, etc., the strength of these solutions being altered through contact with rubber, while the solutions of the alkalies, attacking glass readily, should not be allowed to remain in glass-stoppered burettes after titrations are completed. After use, burettes should be properly washed out and kept filled with distilled water.
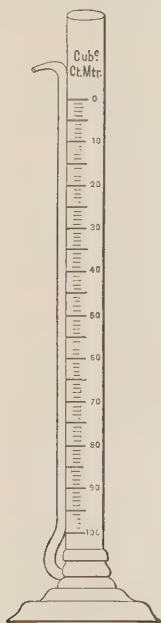

FIG. 7. FIG. 8.
FIGS. 7 and 8. GAY-LUSSAC BURETTES.

The burettes illustrated by Figures 7 and 8, especially that of Gay Lussac, Fig. 8, from which the V.S. is poured out, are interesting forms of measuring devices. They are now obsolete and are little if ever used.

When a standard solution is to be transferred to a burette, the latter should be perfectly dry. Drying of burettes is facilitated by forcing air through them. When not dry, the burette, before filling, is rinsed first with distilled water, then two or three times with small portions of the V.S. and is then allowed to drain, the wash portions of the solution being rejected.

For titration, burettes are secured in a vertical position by clamps (Figs. 9 and 10), made of wood or metal. When the V.S. is discharged from a burette in titrations, the volume is measured from
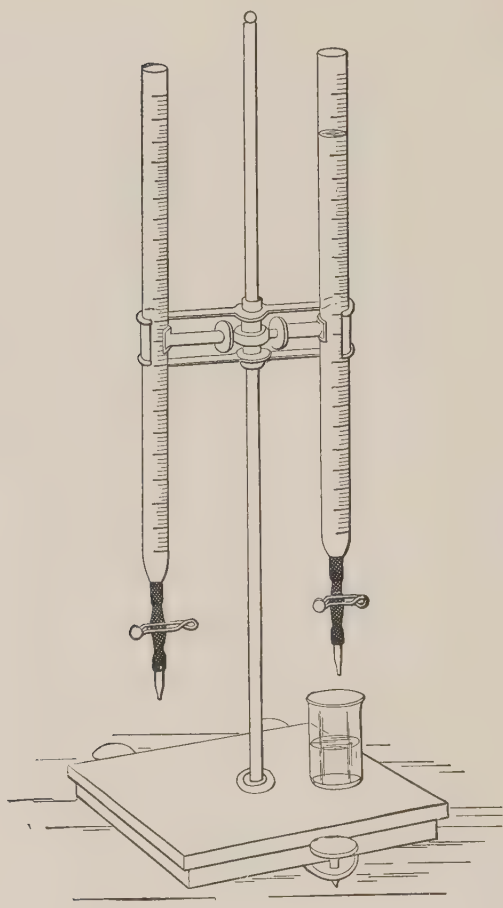
FIG. 9.   BURETTES IN POSITION.

the upper end down; its surface coinciding with the graduation marks on the burette, the volume removed is readily read off.

Reading of Burettes.—Before reading a burette, sufficient time should be allowed for the liquid contained in it to cool, if it is warmer than permissible, and to collect or run off from the surface of the burette. The surface of water or of aqueous solutions in glass vessels is concave; this is easily seen in vessels of small caliber. When viewed in a horizontal plane, the surface presents an appearance illustrated in Fig. 11, known as the meniscus, in which two distinct boundary lines are seen, indicated at *o* and *u,* Fig. 11. Though the volumes indicated by each of these lines will differ, either line may be selected for reading as long as all succeeding readings are made in the same way. The lower dark line of the meniscus, being sharper, is usually preferred for reading. To facilitate reading with ordinary burettes, a white background (a sheet of white paper held behind the burette) is of service, though

a black and white surface will make the lines of the meniscus appear still sharper. Reading with this device is illustrated in Fig. 12, the plate being so held that the edge of the black surface is brought a few millimeters below the surface of the liquid. The
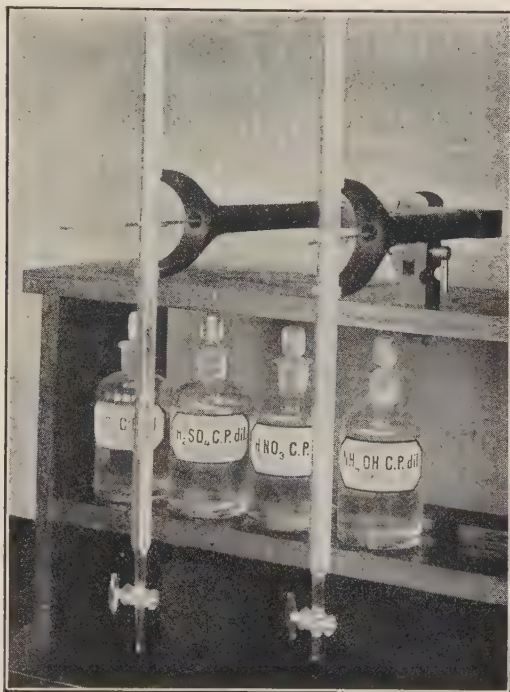

FIG. 10. TUTTLE'S BURETTE SUPPORT.

dark lower line of the meniscus is thus sharply outlined, making reading easier and more accurate. Another device for reading is shown in Fig. 13.

To diminish parallax errors in reading burettes, floats are often employed. These are bulbs of suitable construction to move freely in a burette and are weighed down so as to float in vertical position, Fig. 14. Around the bulb a circular line is etched which, if viewed in a horizontal plane, appears as a straight line. The float changes position with the rise or fall of the liquid in the burette, permitting reading against the circular line around it. There being but a thin layer of the liquid between the float and the burette and a straight instead of a curved line being seen, reading becomes easier and more exact, while measuring of much smaller volumes can be per-
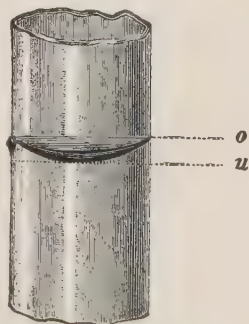

FIG. 11. THE MENISCUS.

formed with accuracy. For dark-colored liquids a two-bulbed float has been devised in which the upper bulb, not immersed in the liquid, serves for reading.

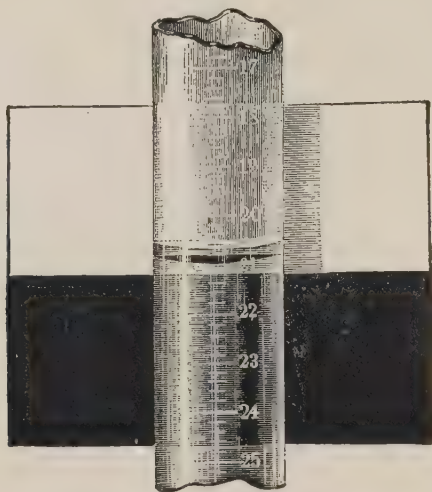Among some of the recent perfections in burette construction is

FIG. 12.   READING A BURETTE WITH THE AID OF A DEVICE.

the production of burettes with opaque backs, known as milk-back burettes. Through the white back passes a straight longitudinal line of dark red or blue color, Fig. 15.   When viewed through the liquid in the burette the dark line appears as a broad band constricted at a point in the meniscus, Fig. 16.   Reading is made against this constricted point and becomes very easy and accurate.

Burettes are usually filled by pouring the solution in through a

FIG. 13.   GOECKEL'S MENISCUS READER.

small funnel, though, like pipettes, they can be filled by drawing the liquid in by suction.   If accidentally overfilled, the solution adhering to the outside of the burette should be carefully cleaned off to prevent its dropping into the titrated liquid.

When many titrations are to be made with the same V.S. it is advantageous to attach the burette to a large container with the

solution from which it can be easily charged. One of a large number of such arrangements devised is pictured in Fig. 18, which represents the burette joined to a syphon, the shorter arm of which extends into the container. Burette and syphon are connected by rubber tubing attached to a T-tube, Fig. 19, inserted between the burette and its tip. The outflow of liquid is controlled by the lower pinchcock, *a,* Fig. 19, the filling of the burette by the upper one, *b,* same figure.

Burettes, which are to hold standard, CO_2-free alkali are best filled by suction and should be closed with rubber stoppers carrying
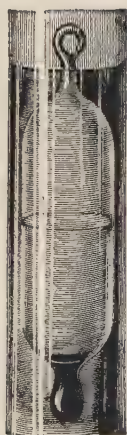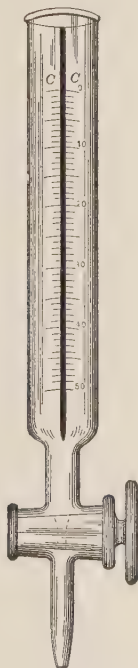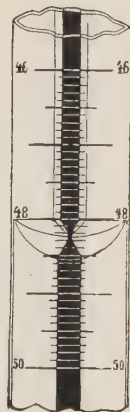

FIG. 14. A FLOAT.   FIG. 15. MILK-BACK BURETTE.

FIG. 16. CONSTRICTION DUE TO REFRACTION OF LIGHT.

soda-lime tubes, such as are used for keeping those solutions. See page 45.

Pipettes.—Pipettes are tubes of small caliber, often bulbed (Fig. 20) into which the liquid to be measured is drawn by suction applied to their upper end. When filled, this end is quickly closed by the finger and the liquid held in; on removing the finger the pipette is discharged. Pipettes are made to hold 1, 5, 10, 20, 25, 100, and even more, cubic centimeters; the larger to simply hold and deliver an exact volume, while the smaller ones are graduated and measure fractions of their capacity like the burettes. The 1 Cc. pipettes are graduated into 0.1 Cc. and into 0.01 Cc. Pipettes are read in the manner described for reading of burettes. When not in use, pipettes are best kept immersed in distilled water. For use, pipettes should be preferably dry; their drying may be hastened by forcing air

3

through them. If not dry, they should be rinsed first with distilled water, then with several portions of the solution to be measured and allowed to drain.

Proper discharging of pipettes is of much importance. See Discharging of Pipettes, page 21.
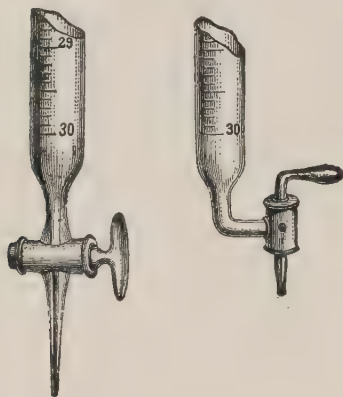
Fig. 17. All-glass Burettes.

Fig. 19. Parts Required for Syphon Connection.

Fig. 18. Burette Connected with a Container.

Cylinders.—Measuring cylinders are graduated vessels standing on a flat base. When provided with a glass stopper they are known as mixing cylinders, Fig. 21. In capacity, they range from 10 Cc. to 1000 Cc. In consequence of their large caliber, measuring with cylinders is not very accurate. Cylinders should be properly calibrated; the smaller ones especially are apt to be incorrectly graduated. These vessels are mostly used for less accurate measurements, mainly to make solutions up to a definite volume, prepare V.S. by mixing, etc.

Measuring Flasks.—The most suitable flasks for measuring solutions are those with flat bottoms and long, narrow necks. Measuring flasks are made to hold, at standard temperature, volumes from 10 Cc. to 2000 Cc. The exact volume a flask will measure is indicated by a circular line etched on the neck of the flask. Sometimes two lines, close together, are found thus marked on the neck, the lower line
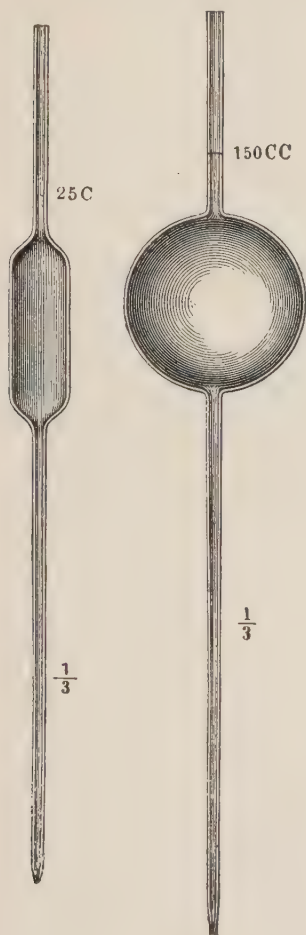
FIG. 20. PIPETTES.
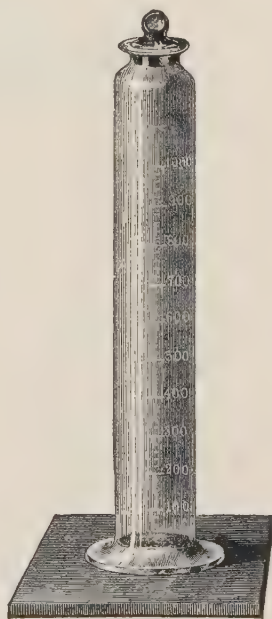
FIG. 21. MEASURING CYLINDER.

then indicating the point to which the flask must be filled *to measure* any fixed volume, while the upper line indicates the point to which the flask must be filled in order *to deliver* that volume. The volume of a liquid occupying the space between the two lines corresponds to the volume of the liquid which remains adhering to the inside of the flask, after the liquid measured has been delivered and the flasks properly drained. Flasks are very serviceable for making

standard V.S., diluting solutions to definite volumes, and measuring larger volumes of liquids accurately.
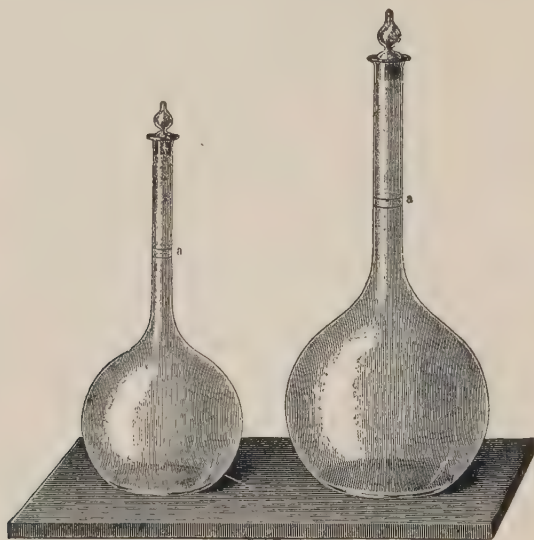
FIG. 22. MEASURING FLASKS.

Calibration of Measuring Vessels.—The accuracy of any measuring vessel or the agreement of a set of such ought not to be assumed. Their adjustment, known as calibration, should be properly made and the corrections, for differences found, applied. Since the volume of a liquid varies with changes in temperature it is necessary to calibrate all measuring vessels at the same standard temperature, preferably 20° C. The capacity of a vessel is found from the weight of distilled water it holds or delivers. The volume of one (1) gramme of distilled water, weighed in air at the standard temperature, is thus established as the unit of volume measure, commonly known as one cubic centimeter or one milliliter. The volume of 1000 Gm. of water weighed in this way is then called a liter. This, of course, is not the true liter which is derived from 1000 Gm. of distilled water at 4° C. weighed in vacuo in a certain locality. However, it is not necessary to employ the true liter in volumetric work, nor would it be practicable to measure liquids at 4° C., the proper agreement of the measuring vessel being alone of importance. The so-called Mohr liter is the volume of distilled water which in air, brass weights used, weighs 1000 Gm.

A flask is calibrated *to hold* any specified volume, say 1 liter, by placing the clean dry flask of the required capacity with 1 Kg. weight on one pan of a strong balance, and counterbalancing them exactly with other weights, pieces of metal, shot, etc., but preferably with a duplicate empty flask and the necessary weights. The 1000 Gm. weight is then removed and distilled water, at standard temperature, poured into the flask until the weights on the other pan are exactly

counterbalanced, care being taken that the outer surface of the flask is dry and no water adheres to the inner surface of its neck above the water surface. The flask is then removed, placed on a level surface and a strip of paper is pasted around the neck so that its upper edge coincides with the lower dark line of the meniscus. To permanently mark the flask, the neck of the emptied and dried flask is covered with a layer of melted wax. When cooled, a fine circular line is cut in the wax with a knife close to the upper edge of the paper, by rotating the flask in its horizontal position, the neck being firmly supported. Solution of hydrofluoric acid is then applied to the groove with a small brush or feather, allowed to act two minutes, washed off with water and after melting, the wax removed by means of paper or cloth.

The exact volume a flask will hold when filled to the mark etched on its neck, is then determined by filling the dry, tared flask with water at standard temperature, and weighing accurately. This should be repeated and the average of the closely agreeing weighings taken.

In order to calibrate a flask *to deliver* a fixed volume, for example 1 Lt., the flask is well rinsed with distilled water, allowed to drain and then calibrated in the manner described. The mark to which it is to be filled to deliver that volume will, of course, be the upper mark.

Discharging of Pipettes.—Filled pipettes may be discharged in several ways. Usually, the larger portion of the liquid a pipette contains is allowed to run out and the remaining small portion is then removed:

(*a*) By shaking out the liquid, in which case a small quantity is always retained in the tip.

(*b*) By forcing the liquid out with air (blowing it out). A drop of the liquid usually holds onto the outer surface. This process is further objectionable on account of the moisture introduced, in blowing out by the mouth.

(*c*) By draining against the side of the receiving vessel or touching the surface of the liquid in it; in this case the outside of pipette should be dry. This method, giving the best satisfaction, should be adopted.

Washing out the contents of a pipette should not be practiced for obvious reasons. Pipettes not being calibrated to hold, like flasks, fixed volumes, the volume of a liquid measured in this way would be greater than indicated. Again, the pipette would retain some of the liquid used for washing out the solution and this would have to be removed before another portion can be measured with it.

Graduated pipettes are easily operated if secured in a vertical position, like the burettes, the upper end being closed by a piece of rubber tubing with a pinchcock.

Calibration of Pipettes.—Pipettes are calibrated only *to deliver* a fixed volume of a liquid. For calibration, a narrow strip of paper is pasted longitudinally on the stem of the pipette above the bulb. Distilled water, at standard temperature, is then drawn in to a selected point which is carefully marked on the paper. The pipette

is then discharged (see method (c), p. 21), into a tared weighing bottle and the exact weight of the water is found. For the second weighing performed, just like the first, the pipette should be filled so that the position of the surface of the water will deviate from the true volume as much as in the first but in the opposite direction. This position is approximately found in the following manner. Let us say that a 10 Cc. pipette, when calibrated, was filled first to a certain mark and the water it held weighed 9.68 Gm. The second filling should weigh somewhat more than 10 Gm. For the third filling the distance between the two marks on the stem of the pipette is divided in correspondence to the two weight deviations from 10 Gm. If necessary, more fillings and weighings are made until the desired point, at which the pipette holds 10 Gm. of water, is found. The exact volume the pipette holds is then found by several trials and the necessary correction registered and applied. The correct mark is then etched on the stem as a circle in the manner described under calibration of flasks.

Calibration of Burettes.—Burettes may be calibrated like pipettes by weighing definite volumes of distilled water, at standard temperature, measured out from them, and noting the correspondence of weight to volume, or, a calibrating pipette, which delivers a definite volume when emptied, is used. The pipette is of about 5 Cc. capacity and after being properly calibrated is attached to the lower end of the burette by a " T " tube in the same manner in which the burette is attached to a large container, Fig. 18. The pipette is then filled from the burette, using the upper stopcock, and is discharged by means of the lower one. By repeated filling and discharging the pipette until the burette is emptied, and carrying this out two or three times, the deviations observed are used to obtain proper averages for corrections.

The agreement, in graduation, of two burettes is readily ascertained by discharging one filled with a liquid to its O mark into the other filled to the highest figure (the lowest mark) of its graduation.

Cylinders are calibrated by measuring into them distilled water from calibrated burettes or pipettes, or, introducing into them definite quantities, by weight, of water at standard temperature, and noting the volumes these occupy.

It is important to have all measuring vessels drain properly so that no portion of the liquid may escape measurement. When a measuring vessel, especially a burette or pipette, is found to retain drops of liquid adhering to its sides, it should be first well washed out with water, next with a strong solution of a caustic alkali, allowing this to remain in it for some time, rinsing with water, and then washing out with a warm solution of chromic acid (potassium bichromate and sulphuric acid), finally washing well with water and allowing to drain.

MANIPULATIONS.

Since in measuring liquids numerous sources of errors are met with, the results of a single titration can not be trusted or accepted

without checking. Duplicate or even more numerous titrations should, therefore, be made. The number of such titrations necessary will depend on the circumstances of the operation, the nature and quantity of the sample, the skill of the operator, etc. Being carried out under the same conditions these titrations should agree closely; this they will do if performed with due care. An average of several closely agreeing volumes obtained is then used for calculation of the results.

To weigh a given quantity of the sample for each titration, separately, in a series of titrations, would consume much time. The practice followed is to weigh a larger quantity of the sample accurately and prepare a definite volume of a solution of it. Aliquot portions of this solution are then carefully measured into the titration flasks. By using the same pipette and draining it in the same manner, the same quantity of the sample may thus be taken repeatedly with convenience and rapidity. Calculations are simplified if the solution of the sample to be divided by measuring is made to measure, in cubic centimeters, a volume 10 times the weight of the sample in grammes; 10 Cc. of such solution will then contain 1 Gm. of the sample. Thus, if 6.54 Gm. of a sample were dissolved and the solution made to measure 65.4 Cc., then 10 Cc. of the solution must contain 1 Gm. of the sample as seen from the following comparison: if 65.4 Cc. contain 6.54 Gm. then 10 Cc. contain 1 Gm.

Direct Percentage Expressions.—When it is desired to obtain, in titrations, a direct percentage expression of the purity of a sample, in Cc. of the V.S. consumed, it is necessary to take for analysis a quantity of the sample which is the exact equivalent of the weight of the reagent present in 100 Cc. of its V.S. Each 1 Cc. of the V.S. will then represent 1 per cent. of the substance. Thus, in the determination of absolute sulphuric acid in a sample of this acid by titration with N alkali, 4.904 Gm. of the sample would have to be used for titration; this quantity of the absolute acid corresponding to 100 Cc. of N alkali. Since that quantity of a 100 per cent. sulphuric acid would consume 100 Cc. alkali, each Cc. of the latter is thus made to represent 1 per cent. of the acid. Now, depending on the strength of the sample, only a certain number of Cc. of the volumetric alkali will be consumed by 4.904 Gm. of it and these will represent the percentage. In some determinations one half or even one fourth of this equivalent quantity is used; 1 Cc. of the V.S. will then correspond to 0.5, 0.25 or any other corresponding fraction of percentage, respectively. This rule holds for both normal and empirical V.S. It must not be overlooked, however, that equivalent quantities are all long fractions and are not easily weighed with accuracy. Further, the quantity of the sample of a substance, whose purity is to be determined, should be sufficiently large to require, were the substance nearly pure, more than a few cubic centimeters of the V.S., but not so large as to make refilling a 100 Cc. burette necessary for one titration. The necessity of this precaution will be realized when it is remembered that in such titrations the smaller the quantity of the V.S. used, the larger will be any possible error due to measurement, end-reaction, etc.

If, for instance, a quantity of a sample be taken that would, to indicate purity of 99.8 per cent., require only 16.2 Cc. of a V.S., then 16.2 Cc. correspond to 100 per cent. and 1 Cc. corresponds to 6.17 per cent. Now, since 0.1 Cc. must be regarded, in ordinary titrations, as the limit of accuracy in measuring, 0.1 Cc. is seen to be equal to 0.617 per cent. Unavoidable deviation of over 0.5 per cent., either way, can hardly be regarded permissible in determination of a required purity of 99.8 per cent.

These methods of adjusting the weight of the sample to the volume of the V.S. to be used for it, simplify determinations and facilitate their execution without sacrificing accuracy, only when judiciously practiced. Considering the advantages gained by a practice which makes weighing and measuring more difficult in order that calculations be made shorter, it must be stated that they appear to be of doubtful value.

Calculations of Results.—When, in the determination, several titrations have been made and their average taken, the data for calculation are then as follows:

Weight of sample used, represented by..........W.
Volume of the V.S. consumed (in Cc.)..........V.
Equivalent quantity of the substance determined which
corresponds to a unit volume (1 Cc.) of the V.S.
= F (factor).

then by proportion:
$$W : F \times V :: 100 : x$$

$$x = \frac{F \times V \times 100}{W} = \text{per cent.}$$

Hence the rule:

Multiply the value of one Cc. of the V.S. which is the quantity of the constituent determined represented by 1 Cc., by the number of Cc. of the V.S. used, then by 100 and divide the product by the weight of the sample (in Gms.) taken.

Direct and Indirect Methods of Analysis.—Volumetric analysis is by *direct* method when the determination is made so that, in titration, the reagent in the V.S. reacts with the substance which is being determined. In the *indirect* method the V.S. is made to react with some product of another reaction, an equivalent quantity of which is produced or set free by the substance sought. Thus, for example, iodine in solution is determined directly by titration with standard sodium thiosulphate, while chlorine, free or available, is first made to act on a soluble iodide and the iodine liberated by it is then titrated with standard thiosulphate V.S. The amount of chlorine in a sample is thus found indirectly through titration of iodine.

Factors.—The quantity of any substance determined which corresponds to a unit volume (1 Cc.) of a standard V.S. is known as the equivalent or factor. For standard solutions of the normal denomination, this quantity is the chemical equivalent of the reagent

based on the unit of valence, and may be readily derived from an equation representing the reaction involved. The factors for the empirical V.S. are obtained from the weight of reagent present, or must be determined by proper titrations.

In this volume the derivation of most of the factors will be given under the individual determinations. Some of these will be found cumbersome fractions, and, while their exact value will be given, some may be advantageously rounded off. This, however, should be left to the prudence of those more familiar with volumetric work; the student is urgently reminded not to alter their value.

Subdivisions of Volumetric Analysis.

1. Determinations by neutralization.
2. Determinations by oxidation and reduction.
3. Determinations by precipitation.
4. Determinations by comparison of colors.

General Maxims.

1. The reaction, on which a determination is based, must be a determinate one. Indeterminate or slowly proceeding reactions are not suited for volumetric methods.

2. Measuring vessels should be properly calibrated; especially should their mutual agreement be as close as possible.

3. Only pure reagents should be employed in volumetric solutions, and the samples to be titrated should be free from substances liable to modify, or in other ways affect, the involved reaction.

4. The exact strength of volumetric solutions at the time of titration must be known. Of the sample, a quantity suitable for titration should be taken and accurately weighed.

5. The temperature of volumetric solutions during titration should not deviate beyond specified limits from the standard temperature adopted.

6. Volumetric solution should be made and standardized at standard temperature and be kept in proper containers, well protected.

7. Weighing and measuring must be accurately performed, and several titrations should be made in order to check results.

CHAPTER II.

DETERMINATIONS BY NEUTRALIZATION.

Neutralization Reactions.

Determinations by neutralization are based on the well-known reaction between acids and bases in which neutral products are formed. This reaction is always an intense one. Just how these substances act and what part those elements, which give an acid or a base its individuality, play in these reactions, has been long unexplained. In recent years, physical chemistry, which, through its theory of ionic dissociation of molecules in solution, has thrown so much light on chemical reactions, advanced an explanation. Whether entirely satisfactory or not, this explanation is found to be a very useful aid in understanding the behavior of the reacting bodies.

Acids are known to be compounds containing replaceable hydrogen (H) and capable of neutralizing bases; just as bases, containing hydroxyl (OH) neutralize acids; the product of this mutual neutralization being a salt. In solution, through the influence of the solvent (water), acids, bases and salts dissociate or ionize, each ionized molecule being resolved into its positive and negative components or ions. The positive ions, called cations, carry a positive charge and the negative ions or anions carry an equivalent negative charge of electricity. Not all soluble compounds ionize. Those that do are known as electrolytes. Of the electrolytes, except in very dilute solutions, only a part of the dissolved molecules exists in ionized state; nor do all electrolytes ionize to the same extent. The extent to which acids or bases ionize determines their strength and is found to vary with the individual acid or base, while salts, with few exceptions, ionize to nearly the same extent.

The ionized condition of a molecule in solution is represented by signs, which indicate the electrical character of the component ions. Cations are marked with the plus ($+$) sign, the anions with the minus ($-$) sign. Thus, to represent hydrochloric acid in ionized state, the symbols used are: $H^+ + Cl^-$; KOH is represented by: $K^+ + OH^-$; KCl as $K^+ + Cl^-$, etc. All acids contain hydrogen (H) ions, all bases have hydroxyl (OH), salts being made up of other ions than these. Thus, acids and bases have, each among themselves, a common characteristic. To what electro-negative ion the positive hydrogens (H) of an acid, or to what electro-positive ion the negative (OH) ions of a base are attached, is immaterial for our consideration of neutralization reactions. In the process of neutralization an acid consumes a base, and vice versa, until one or both are completely used up. But chemical reactions are regarded to take place only between the ionized portions of the reagents, and,

since not all of their molecules present in fairly strong solutions are in the ionized state, it may be asked how can all the non-ionized molecules take part in a given chemical reaction, or, how can all hydrogens of an acid present, be measured by the hydroxyls of a reagent, when only a portion of these are ionized. That the action, in a reaction in which one substance is being neutralized by an excess of the other, does not stop as soon as the ions of the react-ing substances are alone used up, but continues until all, even the non-ionized molecules have reacted, is well known, the explanation of this being based on the theory of an equilibrium which is re-garded to exist in all solutions of electrolytes. When disturbed, through any cause, this equilibrium tends to become reëstablished, thus enabling the reaction to complete itself. Thus, in the case of acids and bases reacting, when some ions of the reagents are used up in production of non-ionized molecules of water, the equilibrium is disturbed and to reëstablish it, more of the non-ionized molecules of the reagents present in solution are forced to become ions. In this manner the disturbing effect on the equilibrium is immediately and continuously followed by additional ionization until a permanent equilibrium results, and the reaction becomes practically completed.

In the reaction of :

$$HCl + KOH = KCl + H_2O,$$

by representing the reagents for the purpose of illustration as com-pletely ionized, the equation becomes :

$$\underset{+}{H} + \underset{-}{Cl} = \underset{+}{K} + \underset{-}{OH} = \underset{+}{K} + \underset{-}{Cl} + HOH.$$
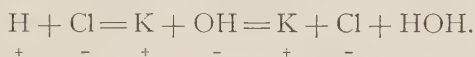
This, of course, is only a partial representation of the changes tak-ing place, yet it shows that the K^+ and Cl^- ions remain as such—water molecules alone being non-ionized—though with increased con-centration of salt in the solution some would become non-ionized KCl. It is manifestly not the formation of a salt that causes an alkali and an acid, reacting, to neutralize each other, nor the attraction of the acid for the base that causes the reaction to proceed, but the cause is to be found in the fact that non-ionized water (HOH), which is composed of the acid and base characteristic ions, is pro-duced in these reactions. It need be stated that water itself is not entirely non-ionizable, but the quantity of its ions is extremely small, having been estimated to be the gramme-equivalent of its ions in one million liters, approximately.

Acids are commonly recognized by their action on coloring mat-ters, turning, for example, blue litmus to red; the soluble bases changing the red color to blue. This characterization can not be rigidly applied, because there exist compounds, not belonging to either of these two groups, which are known to produce a similar reaction in solutions. Some of these, by definition neutral salts, react strongly alkaline, for example: the soluble carbonates, alkali cya-nides, as well as borates and sulphides, while copper sulphate,

mercuric nitrate and other salts in solution have an acid reaction. But these salts of themselves contain neither H^+ nor OH^- ions. How is their behavior to be explained or accounted for?

Since acid and alkaline reaction of a solution is due specifically to the presence in it of H^+ or OH^- ions respectively, the inevitable conclusion is that these ions must be present also in solutions of the named salts. Attention will, therefore, be turned to the solvent, water, which, as was shown, is made up of both of these characteristics of acids and bases. That water shows no reaction is due to the extremely small amounts of its ions. But even were it possible to have an increased concentration of the two ions present, no reaction could be seen, the quantities of these ions being at all times equivalent. Water and some other compounds are, on this account, called amphoteric electrolytes. The part which water plays in imparting to a neutral salt an acid or an alkaline reaction will appear from the consideration, first, of the nature of the salt thus effected. Both carbonates and cyanides of the alkalies are salts of strong bases with weak acids. Taking the simple case for illustration, it will be seen that in an aqueous solution of potassium cyanide, the following will exist:

$$\text{KCN, } \underset{+}{K} + \underset{-}{CN}, \text{ HOH, } \underset{+}{H} + \underset{-}{OH} \text{ (small quantity).}$$
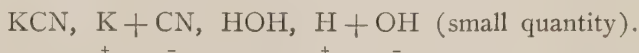
The salt KCN is strongly ionizable, while water is sparingly so; the solution will, therefore, contain a large quantity of CN^- ions, though only few of H^+ ions. But the acid HCN being a weak acid is ionizable to only a slight extent, while the base KOH ionizes strongly, therefore, some non-ionized HCN molecules will be formed with an equivalent amount of those of the ionized KOH. The equilibrium being thus disturbed, to become reëstablished more water molecules are ionized and more of HCN and KOH produced. In this way the concentration of the OH^- ions becomes measurable; the solution reacts alkaline and contains free HCN, mostly in non-ionized state, which may be readily detected by its characteristic odor. The salts of weak bases and strong acids undergo similar changes; their solutions, containing sparingly ionizable bases and strongly ionizable acids, acquire an acid reaction. This action of water on salts in solution is known as hydrolysis.

Ionization of an electrolyte may be increased by: increased temperature, dilution, reduction of pressure, etc. It may be decreased by: decreased temperature, increase of concentration, the presence of an ion in common with the one present, and by addition of other solvents.

Effect on Titrations.—Among the acids and bases the weaker electrolytes are titrated with difficulty, the end reaction being greatly influenced by the presence of the more ionizable salts formed. For their determination, residual titration is resorted to or some other solute, which overcomes the disturbing influence, is added.

INDICATORS.

General Principles.—The indicators used in neutralization processes are coloring matters, both natural and synthetic, which indicate the presence of acid ions (H^+) or of basic ions (OH^-) by the change in color they undergo. The change in color of an indicator is regarded to be due to the changes of its molecules from ionized to non-ionized state, or the reverse, though also to tautomeric changes of the molecules. The least ionizable indicators are the most sensitive; of this there is sufficient experimental evidence.

To be able to undergo changes with minute quantities of H^+ or OH^- ions, an indicator must be either acid or basic in character, though only weakly so for it should, when uncombined, exist in solution in non-ionized state. Indicators are used chiefly in solutions; these should be well protected from dust and light. Solutions of indicators should be frequently examined and, if necessary, their neutrality reëstablished by cautious addition of diluted acid (H_2SO_4), or weak alkali (KOH), so that when five (5) Cc. are diluted with some water, they would respond to four or five drops of $\frac{N}{10}$ alkali or acid V.S.

Test papers of many of the indicators are prepared by saturating neutral filter paper with a solution of the indicator, and drying in a place free from acid or alkaline vapors.

Theory of the Action of Certain Indicators.—Consideration of the action of this kind of indicators is based on the well-known inequality of strength of the individual acids and bases, the acid or basic character of the indicator, and the ionizing action of the solvent.

There are two views, or theories, in existence; the physico-chemical and the pure chemical. The pure chemical theory of the action of indicators considers the changes in color produced by acids and bases to be due to chemical (tautomeric) changes of the molecules of the indicator, while the physico-chemical theory ascribes their action to the existence and behavior of ions in solutions. These two views, heretofore considered as opposed to one another, are now regarded as complementary.

When in a titration an acid is being neutralized by a base, the reaction is considered completed as soon as a minute quantity of the base (OH^+ ions) is in excess. Conversely, the neutralization of a base is regarded complete when an excess of the acid (H^+ ions) has been added. If, then, a coloring matter be present in these solutions which changes color with each of these kinds of ions, the presence of either ion and consequently the end of the reaction would be indicated. But, as indicators generally differ in their behavior, to discuss the physico-chemical theory of their action necessitates that certain of them be considered separately.

One of the best known indicators for neutralization reactions is *phenolphthalein,* a synthetic organic compound of weakly acid character. Being only sparingly soluble in water, the concentration of its ions is unappreciable. In solution, when in the non-ionized state, it is colorless, when ionized, it becomes deep red. In the presence

of acids (H^+ ions), its ionization, low as it is, is even diminished, being, on account of its weak acid character, depressed by acids. Its neutral or acid solutions therefore show no color. With strong bases it forms compounds which ionize readily, the deep red color of its ions appearing as soon as a base (OH^- ions) is present. But the moment the OH^+ ions are removed by the addition of an acid, the molecules of the indicator are set free by the acid, and not ionizing, the red color disappears. These changes are sharp, even with weak acids but with only strong bases. This peculiarity is believed to be due to the fact that a weak base, like ammonium hydroxide, does not readily combine with the weakly acid phenolphthalein; any compound formed in small quantity undergoing hydrolysis[1] so that the red ions are not readily produced except by a large excess of the weak alkali. An excess of a weak base is not readily indicated by phenophthalein and the end-reaction, for this reason, is not reliable. But weak acids, even H_2CO_3, H_2S, H_3BO_3, although relatively strong when compared with the indicator's acid powers, readily decompose the ionizable salts of phenolphthalein with strong bases and discharge the red color. This behavior points to the usefulness of this indicator for the determination of weak acids and strong bases.

Methyl orange, another valuable indicator, behaves somewhat differently. Methyl orange is a synthetic organic acid of medium strength used as the sodium or ammonium salt; its molecules in solution are pale red, its ions being intense yellow. Unlike phenolphthalein it is ionized somewhat more itself so that its pure water solution, which is of orange color, becomes yellow on dilution. On this account its changes in color lack sharpness. It reacts readily with even the weak bases, the salts formed ionize and the yellow color of its ions is visible. Strong acids decompose the salts formed, and the free, non-ionized molecules impart to the solution a red color. Weak acids, however, can not decompose the methyl orange salt, or do so only imperfectly; the color changing only when a large excess of the weak acid has been added. This behavior shows that methyl orange is useful in titration of all, even weak bases but only the strong acids.

The difference in action of these two indicators is illustrated by their behavior in titrations of other than monobasic acids. For example, carbonic acid, when titrated in solution acts toward phenolphthalein as a monobasic acid, the red color of the phenolphthalein ions appearing when the acid has all been converted into a bicarbonate. But the same acid has no effect on methyl orange except when present in very large quantities. Phosphoric acid, when titrated with an alkali, is dibasic with phenolphthalein, the alkali added not affecting the indicator until two hydrogens of the molecule of the acid are replaced. The product of the reaction, Me_2HPO_4 is evidently not basic enough to combine with the indicator. With methyl orange, phosphoric acid is monobasic; the yellow color pro-

[1] In view of the other theory, phenolphthalein forms colorless salts, the colored ones being their tautomeric forms, the change being from benzenoid lactone to quinonoid carboxylic form.

duced by OH ions appearing when one of the acid's three hydrogens has been replaced. The Me_2HPO_4, which then starts to form, is sufficiently basic to combine with this indicator and cause its ions to appear.

Most indicators besides differing in their properties, such as solubility, color, ionizing power, basic or acid character, exhibit marked differences in their sensitiveness to acids and bases and, on this account, are variously classified. The grouping of Glaser, being based on their relative sensitiveness as well as other properties, is deemed of practical value and is here given to serve as a guide to their selection, though Wagner's chemical classification is also presented.

CLASSIFICATION OF INDICATORS USED FOR NEUTRALIZATION REACTIONS.

I. Chemical Classification of Wagner.

A. Indicators with the characteristic ion univalent:
    1. Containing anion.
    2. Containing cation.
B. Indicators with the characteristic ion polyvalent:
    1. Containing both anion and cation (amphoteric electrolytes).
    2. Containing uni- or polyvalent anions or cations.
Class A, 1. Iodeosin, cochineal, flavescin, alizarin, orseille, p-nitro-phenol, rosolic acid, tropæolin OOO, curcumin W (curcuma), fluorescin, litmus, lacmoid phenolphthalein, Poirrier's blue.
These are the more sensitive the weaker their acid character.
Class A, 2. Methyl violet, dimethyl amido-azobenzol.
Class B, 1. Tropæolin OO, Congo red, benzopurpurin, methyl orange, ethyl orange.
Give intermediate colors on account of the presence of both ions.
Class B, 2. Alizarin-sulphonic acid, gallein, hematoxylin, phena-cetolin.

II. Practical Classification of Glaser.[1]

Group 1.—In this group the indicators are either pronounced acids, or very weak bases. The latter form ionizable compounds only with strong acids, these compounds decomposing in the presence of even weak bases, while the former, themselves acids, readily react with the weak bases. Their special value as indicators for titration of bases is thus apparent. For acids they are available only when the acids are strong. They are arranged in the order of their sensitiveness.
Iodeosin, tropæolin OO, *methyl orange,* Congo red, benzopurpurin, cochineal, lacmoid.
Group 2.—Into this group belong all indicators of weakly acid character. They readily unite with bases to form unstable salts which even weak acids decompose readily. They are, therefore,

[1] Glaser, Indicatoren der Acidimetrie und Alkalimetrie.

better adapted for the titration of acids than of bases, though they are employed for both.

>Fluorescin, phenacetolin, hematoxylin, gallein, alizarin, orseille, *litmus,* p-nitrophenol.

Group 3.—Indicators of still weaker acid character than the preceding are included in this group. They unite readily with only the strong bases, the compounds thus formed are decomposed by even weak acids. They are very sensitive to acids, but not to bases except when the bases are strong.

>Rosolic acid, tropæolin OOO, curcuma (curcumin W), flavescin, *phenolphthalein,* a-naphtholbenzoate.

Comparison of Indicators.—The comparative acidity of two indicators, when required for the purpose of classification, is found by careful titration of their solution, acidified with HCl, with $\frac{N}{10}$ KOH V.S. Those of stronger acid character change color before the weaker ones. By reversing the titration the order of the changes in color is also reversed.

Effect of Indicators on Results in Titrations.—It would be natural to suppose that identical results can not be obtained with indicators belonging to different groups when used for the titration of the same substance and the same V.S. being used. This has been fully confirmed by practice. If, for example, 10 Cc. of an acid require, with methyl orange, 9.9 Cc. of a standard alkali, with phenolphthalein 10.1 Cc. of the same V.S. must be used. The salt of methyl orange ionizes, has alkaline reaction and therefore neutralizes some acid itself, while the phenolphthalein being weakly acid requires alkali to be consumed in order that its red ions be produced.

The Order of Titration.—When two V.S., alkali and acid, are titrated one by the other as in their standardization, using the same indicator, two results, depending on the order of mixing, are obtained. The end-reaction produced by an excess of either the acid or the alkali V.S. will be correct only when titrations are made with the same V.S. In standardizing V.S. the order of titration will depend on the nature of the indicator as may be seen from the following:

a. Titration of an acid with alkali; both in $\frac{N}{10}$ V.S.

>10 Cc. of acid, with methyl orange require   9.9 Cc. alkali **V.S.**
>10 Cc. of acid, with phenolphthalein require **10.1 Cc. alkali V.S.**

b. Titration order reversed; volumetric solutions the same.

>10 Cc. of alkali, with methyl orange require 10.1 Cc. of acid **V.S.**
>10 Cc. of alkali, with phenolphthalein require 9.9 Cc. of acid **V.S.**

It will be observed that concordant results may be obtained with these two indicators only by titrating in the reversed order.

Effect of Light and Heat on Titrations.—Some indicators, methyl orange, phenolphthalein, cochineal, Congo red, for instance, may be employed for titration in artificial light, others can not be so used. At best, titrations in artificial light, which is known to be much varied in color and intensity, are not reliable and should not be practiced; best results require good daylight.

Few indicators permit titrations in hot solutions; most of them, however, are decomposed by heat or are made insensitive.

The Quantity of an Indicator.—As a rule, only as much of an indicator as required to impart color to the titrated liquid should be used. The solutions of indicators are usually made of such strength

FIG. 23. SCHUSTER'S DROPPER.

FIG. 24. DROPPING BOTTLE.

that two to five drops, added to 50 Cc. of distilled water, give sharp changes of color with a drop or two of $\frac{N}{10}$ V.S. The stronger than $\frac{N}{10}$ V.S. will then react very sharply with this quantity of the indicator but, for the weaker V.S. ($\frac{N}{50}$ or $\frac{N}{100}$), the quantity of the indicator must be reduced. The need for this will be apparent from consideration of the acid or basic character of the indicators spoken of under their classification. For dropping of indicators suitable dropping bottles are employed. See Figs. 23 and 24.

Concentration of the Titrated Solution.—Since in titrations the changes in color do not depend on the quantity of the indicator present—smallest possible amount being used—nor on the quantity of the H or OH ions of the reagents added—the smallest possible excess being aimed at—it is evident that the concentration of the solution of the titrated substance becomes an important factor. The solutions should, therefore, be of nearly the same concentration in determinations as they are in standardization of the V.S. employed for them.

Interference with Indicators in Titrations.—Some substances, of themselves neutral, are known to interfere with the action of indicators when present in the titrated liquid. Alcohol and acetone are the more common non-ionizing solvents which act in this way when present in larger quantities (strong concentrations). Ammonium salts, being decomposable by alkalies and also those of zinc, magnesium, aluminium, chromium, tin and other metals, which form hydroxides with alkalies, will be found to interfere. When in titrations, precipitates are formed, these are apt to carry down the indicator in combination with them or through adsorption. Other soluble salts not giving precipitates, if present, will often affect the accuracy of the end-reaction. When practicable, such interfering agents should be removed previous to a titration, or

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if that can not be readily done and a distinct end-reaction can be obtained in their presence, an equal amount of such substance should be titrated in a blank.

DESCRIPTION OF INDICATORS.

PHENOLPHTHALEIN. $C_{20}H_{14}O_4$.

Bases = red.   *Acids = colorless.*

Solution employed: 1 per cent. in alcohol. (U.S.P. Test Sol. contains dil. alcohol.)

Properties.—A synthetic organic compound of weakly acid character prepared from phthalic anhydride and phenol in presence of strong sulphuric acid. It is sparingly soluble in water, very soluble in alcohol to a colorless solution. Phenolphthalein ionizes to but a small extent; the non-ionized molecules are colorless, the ions have a red color. Traces of a strong base produce this red color when allowed to come in contact with it in solution. The base forms with it an ionized compound though a very large excess of it destroys the red color. Acids discharge the red color by their reaction with the ionized compound in which the colorless, non-ionized molecules of the indicator are regenerated. Phenolphthalein is very sensitive to most acids: The organic acids as well as the weak inorganic acids like HCN, H_2S, H_2CO_3, $B(OH)_3$, etc.—but not H_2SiO_3—when brought in contact with it in solution decompose its feeble combinations with bases, and discharge the red color of its ions. With weak basic compounds, such as Na_2HPO_4, $Al(OH)_3$, $NaHCO_3$, NH_4OH, etc., it gives no reaction or reacts very imperfectly and can not be employed for their titration.

Uses.—Phenolphthalein is very useful for titration of acids including the organic, and for strong bases. Ammonium salts, when present in the titrated liquid, diminish its sensitiveness. As the end-reaction, the production of a pink color by titration with an alkali V.S. is more readily detected, and the excess of V.S. controlled, than the discharge of the red color by an acid, although this is quite contrary to the sensitiveness of the indicator. Phenolphthalein works well in artificial light and may be used in boiling solutions. Boiling with strong alkalies destroys it. Alcohol and acetone, when present in the titrated liquid, interfere with its sensitiveness.

Phenolphthalein Paper.—Pure, unsized paper is immersed in the alcoholic solution of the indicator (see above), and after drying in a place free from dust and reactive vapors, is kept in a well-closed bottle. Its uses are limited to detection of alkalies in solutions, and as indicator for those titrations in which it is necessary or desirable to ascertain the end-point outside the titrating vessel.

METHYL ORANGE.[1] $(N(CH_3)_2 — C_6H_4 — N = N — C_6H_4SO_3H.)$

Bases = yellow.   *Acids = light red.*

Solution employed: 0.1 per cent. in water. To the aqueous solution, $\frac{N}{10}$ sulphuric V.S. is added until it becomes turbid and red; it is then filtered.

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[1] Also known as helianthin, Poirrier's orange III. or mandarin orange.

Properties.—An organic acid, the dimethyl azobenzene sulphonic acid. The indicator commonly employed is really the sodium or potassium salt. The free solid indicator is violet-colored, the salts are orange. Completely soluble in water, the solution except when very dilute, is of orange (not brown) color, changing to cherry red with strong acids and to deep yellow on addition of a base. A hot, concentrated solution of the salt deposits on addition of an excess of HCl lustrous, violet plates (should not be brown). With few drops of gold chloride solution a red color is produced but no reaction should be seen when calcium or barium chloride is added. Methyl orange is an acid[1] of moderate strength and therefore ionizes in solutions. Its ionization is increased by bases and depressed by acids. With bases it readily combines to form salts which however are decomposed only by strong acids; hence its greater sensitiveness to bases. Bases, including the weak ones, such as the Ca, Sr, Mg and NH_4 hydroxides, methyl and ethylamines, morphine and quinine, but not pyridine, aniline, toluidine, combine with it and may be titrated in its presence. Organic acids and the weak inorganic H_2CO_3, H_2S, HCN, As_2O_3, $B(OH)_3$, etc., either do not react with it or react only incompletely. This indicator is, therefore, not suited for their titrations. Ferric, aluminium, chromium salts, the hydrosulphides and soluble bicarbonates do not affect it. Phosphoric and sulphurous acids act as monobasic acids towards it, the end-reaction taking place when one hydrogen of the molecules of these acids has been replaced by a metal. Soluble carbonates, bicarbonates, aluminates, deport themselves as bases toward methyl orange and may be titrated as such in its presence. The alkali sulphates and ammonium salts diminish its sensitiveness while nitrous acid (in HNO_3) destroys its color. In such cases more of the indicator should be added when the end-reaction has been nearly approached.

Uses.—On account of its greater sensitiveness to bases, methyl orange is employed for the determination of these and of only the strong acids. The end-reaction with a V.S. of the alkali is the more delicate; to most eyes, however, the change from yellow to red is much easier to detect than the reverse change. Titrations are, for this reason, often finished with a strong acid V.S. though that is contrary to actual delicacy of the end-reaction. Methyl orange should not be used in hot solutions. In artificial light it gives satisfactory service. The volume of the titrated solution should, particularly with this indicator, be kept nearly equal to that of the diluted V.S. employed in the standardization of the V.S. used. Of the indicator only a minimum quantity, or just enough to impart to the solution a distinct color, should be employed. For accurate results the titration with methyl orange should be carried out to the transition orange tint, as the end-reaction. One drop of the V.S. should then change the color either to red or yellow.

Note.—For light colored (yellow) liquids the addition of indigo to methyl orange is recommended by C. Luther. The end-point is then indicated by a grey transition tint, or since there is a succes-

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[1] Though also regarded a base; the ions are claimed to be red, the non-ionized molecules yellow.

sion of colors produced which includes yellow, green-grey and violet, any one of these may be selected for the end-point.

Methyl Orange Paper, Yellow.   Methyl Orange Paper, Red.— These papers are prepared from the respective alkaline and acid solutions of the indicator obtained by cautious addition of the corresponding $\frac{N}{10}$ V.S. They serve the same purpose as the phenolphthalein paper, q. v.

LITMUS.

Bases = *blue.*   *Acids* = *red.*

Properties.— The pigment is obtained from certain lichens (*Rocella tinctoria, R. fuciformis,* etc.). Commercial litmus varies considerably in quality—usually contains chalk and gypsum—and in sensitiveness. As an indicator, its value depends on azolitmin, one of the color principles present in it. Azolitmin may be isolated and employed in place of the usual solution of litmus. To prepare a solution of the indicator, powdered litmus is macerated with boiling 95 per cent. alcohol to dissolve and remove from it the objectionable coloring matter, chiefly erythrolitmin. Three to four successive macerations, each lasting one hour and made with as much alcohol as the quantity of the sample, will extract all the undesirable constituents, any adhering alcohol being, after extraction, washed out with cold water. The residue is then extracted with five parts of boiling water, the solution thus obtained cooled and filtered when cold.

·A solution of litmus kept away from air deteriorates, turning red on account of the activity in it of anaërobic microörganisms. By giving air a free access, this decomposition of the solution may be prevented ; the bottle in which the solution is kept should be closed with a plug of cotton to keep out the dust.

With acids, litmus gives a red color which bases change to blue ; the transition color is violet. The solution of the indicator should be nearly neutral and should, when 5 drops of it are added to 50 Cc. of distilled water, change color with one drop of $\frac{N}{10}$ alkali or acid V.S. If necessary, its neutrality should be carefully reëstablished. Neutral salts, nitric acid, nitrous and sulphurous acids, and hydrogen peroxide, do not interfere with its use as indicator in titrations. In artificial light litmus gives good results, the color changes appearing especially sharp if observed in sodium light ; the red of acids then appears colorless and the blue of bases becomes blue-black.

Uses.—Litmus occupies a position (see classification) between phenolphthalein and methyl orange, and as its properties indicate, is serviceable for titrations of the strong mineral acids and nearly all bases including ammonium hydroxide. It works well in the presence of oxalic and formic acids.

Litmus Paper, Blue.—Large strips of purified, white filter, or other unsized paper are immersed in the blue solution of litmus and then dried, suspended in a place free from dust, acid and ammoniacal vapors.

Litmus Paper, Red.—Prepared like the blue paper. The red litmus solution is prepared from the blue by careful addition of very dilute hydrochloric acid until a red tint is just produced.

Litmus Paper, Neutral.—Litmus solution for this paper is readily provided by mixing the two solutions, red and blue, in such proportions as to produce one of neutral or violet color.

To be sensitive, the blue and the red papers must not be intensely colored. When dry, these test papers are cut into suitable narrow strips and are kept well preserved for use.

Azolitmin, is a dark brown powder, sparingly soluble in water, insoluble in alcohol or ether. With bases it gives soluble salts of blue color, which acids turn red. For use, a 1 per cent. solution in water is prepared and made just blue with $\frac{N}{10}$ KOH V.S. High price is the only objection to its use in place of the solution of litmus.

Phenolphthalein, methyl orange and litmus are by far the most valuable indicators out of the rather large number used, or recommended for use, in neutralization reactions. With the exception of the alkaloids, the determination by titration of any acid or base may be made without the use of any other indicator. Their selection for specific purposes has been set forth in their classification and detailed under their description. Briefly summarized, the indications for these indicators are:

For strong bases and most acids
    including the organic......Phenolphthalein (may be boiled).
For strong mineral acids and
    most bases, even the weak..Methyl orange (in cold solutions),
For most mineral acids
    and nearly all bases......Litmus or azolitmin (cold or boiling).

OTHER INDICATORS.

Alizarin.—Diazoanthraquinon. $C_{14}H_8O_4$.

Bases = red,   *Acids = yellow.*

A solution of 0.5 Gm. in 100 Cc. of alcohol is employed. The end-reaction is sharper when the titration is finished with an alkali V.S. May be used in artificial light.

Alizarin (S).—Sodium alizarin sulphonate. $C_{12}H_9O_3N$.

The end-reactions are the same as those of alizarin. This salt is, however, more sensitive to alkalies and less to acids than alizarin, and gives in addition a red color with phosphoric acid or MeH_2PO_4, while with the neutral phosphates violet color is produced.

Benzopurpurin (B).—$C_{34}H_{26}N_6(SO_3H)_2$.

Bases = red.   *Acids = violet.*

Benzopurpurin acts like Congo red, q. v. To be employed as indicator the commercial article should be purified. This is usually effected by precipitating it from solution with HCl and drying on water-bath without washing. To prepare a solution, 0.5 Gm. of the powder is suspended in water and sodium hydroxide solution

added until dissolved, the solution, however, retaining a slight acid reaction (violet color). Benzopurpurin is of value for the detection of minute quantities of ammonia in air. Paper, moistened with the solution and exposed to traces of ammonia, becomes violet-blue on drying.

Cochineal.

Bases = violet.   *Acids = yellow-red.*

A tincture of the unbroken insect is made by macerating 3 Gm. of cochineal in 250 Cc. of 25 per cent. alcohol during several days and filtering. The indicator thus obtained is of acid reaction and must be carefully neutralized before use, with very dilute ammonium hydroxide. Cochineal is valuable for titration of most bases, including NH_4OH, but especially of the *alkaloids*. It may be employed in titrations of the inorganic acids but it is useless for the organic. Salts of iron, aluminium and copper, when present, impair its sensitiveness; boiling alkalies destroy it. It works well in alcoholic solutions. In place of the tincture a 1 per cent. solution of the coloring principle of cochineal, carminic acid ($C_{17}H_{16}O_{10}$) is sometimes used.

Congo Red.—Sodium diazo benzidin naphthionate.
$$C_{32}H_{22}N_6(SO_3Na)_2.$$
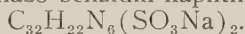
Bases = red.   *Acids = blue.*

Red-brown, soluble in water and in alcohol. To prepare a solution of this indicator, 0.5 Gm. of it is dissolved in 90 parts of water and 10 parts of alcohol added. Useful for inorganic acids and most of the bases, including the more basic alkaloids. Neutral salts of the alkali and alkaline-earth metals, when present in a large quantity, make its color changes indistinct. Nitrites destroy it but H_2S and H_2SO_3 do not affect it. Titrations in which Congo red is used should be finished with the alkali V.S. Not to be employed in hot solutions.

Corallin-Malachite Green.

Bases = purple.   *Acids = green.*

Yellow corallin, which is a mixture of many substances, is used as an indicator, like rosolic acid. To make it available for titrations of colored liquids (wine, cider, vinegar, etc.) the addition of malachite green has been recommended.[1] A solution of 3.1 Gm. of corallin, or commercial rosolic acid in 150 Cc. of 96 per cent. alcohol is prepared, neutralized, and to the solution is added 0.5 Gm. of malachite green, dissolved in 50 Cc. of alcohol.

Curcumin (W).—$C_{26}H_{18}O_2H_4(SO_3Na)_2$.

Bases = red.   *Acids = blue.*

Solution of 0.2 Gm. of the salt in water has a greenish color and is employed like turmeric, q. v.

[1] E. G. Runyan, J. A. Chem. Soc., 1901, p. 402.

Fluorescin.—$C_{20}H_{14}O_6$.

Bases = yellow-green fluorescence.   Acids = yellow.

Dark yellow crystalline compound prepared from resorcin and phthalic anhydride.   Sparingly soluble in water and in dilute alcohol; readily soluble in acetic acid.   For use, to 0.05 Gm. of fluorescin dissolved in 50 Cc. alcohol are added 50 Cc. of water. The indicator is very sensitive to alkalies in alcoholic or in ethereal solutions.   One drop of a $\frac{N}{10}$ V.S. of an alkali produces a distinct fluorescence.   Salts of the alkalies do not affect it, but those of the alkaline-earth metals diminish its fluorescence.   It is most sensitive when used in aqueous or alcoholic solutions covered with ether. In titrations with fluorescin, the titrated liquid must be clear, as any turbidity interferes with the sensitiveness of the end-reaction, and must be viewed in reflected light against a black background.   The indicator is very serviceable for titrations in colored liquids, such as the solutions of alkaloidal residues; it may be used in hot solutions.

Gallein.—(Cœrullin.) $C_{20}H_{10}O_7$.

Bases = bright red.   Acids = light brownish-yellow.

A condensation product of phthalic anhydride and pyrogallol. Occurs as greenish crystals or red-brown powder, soluble in alcohol, sparingly soluble in ether.   Used as 1 per cent. solution, 1 part being dissolved in 50 parts of alcohol and the solution diluted to 100 with water.   Employed in titration of alkaloids.

Hematoxylin.—$C_{16}H_{14}O_6$.

Bases = violet to purple.   Acids = yellow-orange.

A yellow crystalline principle obtained from logwood (Campechy wood).   It is insoluble in water, soluble in alcohol.   Exposed to air its color darkens.   Solution of 0.2 Gm., in alcohol 100 Cc., is employed as indicator.   With $Ba(OH)_2$ solution blue color is produced. Hematoxylin is suitable for titration of strong acids and bases and is recommended for some alkaloids.   In artificial light, especially the yellow light of sodium, its color changes are readily distinguishable. It also serves as an extremely sensitive reagent for copper in solution; 1 part of Cu in billion is said to give blue color with it.   A tincture of logwood has been employed in place of hematoxylin.

Iodeosin.—Tetraiodofluorescein. $C_{20}H_8I_4O_5$.

Bases = pink.   Acids = colorless.

Brick-red powder, soluble in alcohol, acetone, and only sparingly soluble in water or in ether saturated with water; insoluble in pure ether or benzole.   For common titrations, a solution of 0.1 Gm. in 100 Cc. of alcohol is employed.   It is very sensitive to bases with which it gives a pink color.   Acids discharge the color on thorough shaking.   For 100 Cc. of the titrated liquid about 5 drops of the indicator are used.   If an alkaloidal residue is to be titrated, its solution in standard acid is diluted to measure 100 Cc.   To the acid liquid 20 Cc. of ether are added, the mixture well shaken and

then titrated with a standard alkali V.S. of which small portions
are run in, shaking after each addition until the aqueous layer takes
on a distinct pink color, the shaking towards the end of the titration
should be more vigorous. To detect or estimate minute quantities
of alkalies (such as dissolve out of glass), an ethereal solution of
the indicator is employed which is prepared by dissolving 0.002
Gm. of iodeosin in 1000 Cc. of neutral ether previously saturated
with distilled water. Titrations are best performed in closed cylin-
ders. These cylinders or other titration vessels should, before use,
be washed out by boiling distilled water in them for several hours.
Employed for the weaker alkaloids. Phosphoric acid is monobasic
with iodeosin, giving, it is claimed, a sharp end-reaction. With
barium hydroxide V.S. it should not be employed. Works best in
an alcoholic solution.

Lacmoid.—Resorcin blue. $C_{12}H_9O_3N$.

$\qquad$ *Bases $=$ blue.* $\qquad\qquad\qquad$ *Acids $=$ reddish.*

Lacmoid is prepared from resorcin and sodium nitrite. It is
insoluble in alcohol, acetic acid, acetone or phenol; sparingly solu-
ble in water or in ether; insoluble in chloroform, petroleum, ether or
benzol. The commercial article is mostly impure and often entirely
unsuited for use as an indicator. Good specimens of it color water
intensely blue, the alcoholic solution being blue-violet, but not brown.
To prepare a solution, the selected sample is dissolved in 12 parts
of 20 per cent alcohol, the solution filtered and evaporated in vacuo
over sulphuric acid. Of the residue thus obtained, 0.2 Gm. is then
dissolved in 100 Cc. of 96 per cent. alcohol for use. Lacmoid resem-
bles litmus in properties and reactions, though it is more sensitive
to bases than to acids, permitting the employment of very weak
alkali V.S. Used for the titration of strong acids and most bases
including ammonium hydroxide. Nitrous acid interferes with its
sensitiveness.

Orseille.

$\qquad$ *Bases $=$ violet.* $\qquad\qquad\qquad$ *Acids $=$ red.*

In certain lichens the principal coloring matter is orcein, the
mother substance of the coloring principles of litmus. Solution of
it is prepared by digestion of 5 Gm. of orseille in 95 per cent. alcohol
during two hours on water-bath, filtering and making solution up
to 100 Cc. The rose-red solution is not changed by acids but gives,
with bases, a violet color.

Paranitrobenzen.—Azo-a-naphthol sulphonic acid.
$\qquad\qquad$ ($NO_2C_6H_3SO_3H \cdot N = N \cdot C_{10}H_6OH$.)

$\qquad$ *Bases $=$ purple.* $\qquad\qquad\qquad$ *Acids $=$ yellow.*

This indicator is said to resemble phenolphthalein in its action
(J. T. Hewit, Analyst, 1908, 33, 85), acting in hot or cold solutions,
from which it, however, differs in that its color changes are not
affected by acetone or alcohol, and an excess of an alkali does not
destroy the purple color.

Note: Paradimethyl-aminoazobenzene-o-carboxylic acid, styled "methyl red," has been recommended as a very sensitive indicator to alkalies by Rupp and Loose, permitting the use of $\frac{N}{100}$ V.S. It is almost insoluble in water but more soluble in alcohol; a 0.2 per cent. alcoholic solution is employed. With bases = yellow; acids = violet-red. Suitable for weak bases, ammonium hydroxide and certain alkaloids included.

Paranitrophenol.—$C_6H_5O_3N$.

Bases = yellow.   *Acids = colorless.*

A solution of 0.2 Gm. in 100 Cc. of alcohol is made and sometimes used. The indicator will stand boiling temperatures.

Phenacetolin.

$Bases \begin{cases} hydroxides = yellow. \\ carbonates = red. \end{cases}$ *Acids = yellow.*

Phenacetolin is prepared from phenol and acetic acid. It is a yellow-brown powder, soluble in alcohol. One per cent. alcoholic solution is employed. Very sensitive to alkali carbonates with which it forms a salt of red color; with the hydroxides a basic compound of yellow color is formed. Works well in artificial light and in hot solutions. Most neutral salts do not affect it, though ammonium salts make its end-reactions lack sensitiveness. Useful in titrations of alkali hydroxides and carbonates when present together. In such determinations it gives somewhat higher values for the carbonate, with proportionally lower values for the hydroxide.

Rosolic Acid.—(Methyl aurin, Pararosolic acid.) $C_{20}H_{16}O_3$.

Bases = violet-red.   *Acids = yellow.*

Rosolic acid is derived from rosanilin. A ruby-red crystalline substance with greenish refraction, insoluble in water, soluble in dilute alcohol. For use, 1 Gm. is dissolved in 10 Cc. of alcohol and the solution diluted to 100 Cc. with water. It is sensitive to most acids, acetic and phosphoric being excepted. Strong bases may be titrated in its presence; ammonium hydroxide only in considerable dilutions. Color changes are readily seen in green light. Ammonium salts, when present, interfere with its sensitiveness. Rosolic acid is employed to detect bicarbonate in milk. Aurin ($C_{19}H_{14}O_3$), which is its homologue, and corallin, a mixture of many compounds, are often employed in place of the acid.

Tropaeolin (OO).—Sodium phenyl amido azobenzol sulphonate (Orange IV). $C_{18}H_{14}N_3(SO_3Na)$.

Bases = yellow.   *Acids = orange-red to violet.*

Dark shiny needles, somewhat soluble in water, readily soluble in alcohol. Test solution made by dissolving 0.05 Gm. in 100 Cc. of alcohol has a reddish-violet color. This indicator is not extensively used in titrations, its end-reactions being rather uncertain. Employed like its isomer, metanyl yellow, to detect inorganic acids (in vinegar, for instance). For this, dry test papers are made.

Tropaeolin (OOO).—a-naphthol azobenzene sulphonic acid.
(Orange I). $C_{16}H_{11}ON_2(SO_3H)$.

Greenish-black shining leaflets. Suitable for titrations of most acids and strong bases, but is little employed.

Turmeric.

Bases = brown.   *Acids = yellow.*

A tincture of turmeric (Curcuma longa) is prepared by digesting the powdered root with several portions of water, rejecting these extractions and drying the residue. The residue is then macerated in six parts of alcohol during several days and the mixture filtered. The tincture and the test paper made from it are employed chiefly as reagents for boric acid. Boric acid, or borates, in the presence of a minute quantity of HCl, on drying give, with turmeric, a characteristic cherry-red color. Ammonium hydroxide changes this color to bluish-black.

Volumetric Solutions.

Preparation and Standardization.—It has already been stated that a reagent to be available for standardization of volumetric solutions, must fulfill certain rigid requirements. Definite chemical composition, stability in air, readiness of purification, solubility in water, sharp end-reaction and inexpensiveness were especially insisted upon.

Native calcium carbonate (calx spar, Iceland spar) which occurs crystalline and quite pure, was for a long time relied upon as the source of standard V.S. For this purpose it is still found very useful though it fails to fulfill some of the demands enumerated. It is very stable but does not permit of ready purification and is insoluble in water. It is chiefly on account of its insolubility that it could not be retained as the source of standard V.S., other substances not handicapped in this respect having been adopted. One of those lately adopted reagents is potassium bitartrate, an acid salt which neutralizes bases and, being readily purified, has found favor with many. The U.S.P., 8th Rev., adopted it as the standardizing agent for its V.S. and gives a detailed method for the purification of this compound. But as a source of standard V.S., anhydrous sodium carbonate is perhaps the most widely employed reagent, though sodium oxalate, dehydrated at 240° C. gives entire satisfaction and is highly recommended by many. However, there are many other agents, whose number is constantly increasing, that are finding favor and preference with others. Among these only the more common ones can be named. Oxalic, hydrochloric, succinic,[1] benzoic, salicylic and cinnamic, arsenous acids; ammonium chloride, sulphate, triiodate; potassium diiodate, dichromate, trioxalate; borax, calcium oxide, pure silver and many others. The purity

[1] Succinic acid and its anhydride, benzoic and phthalic anhydrides, were studied as sources of standard V.S. by T. K. Phelps and L. H. Weed (Am. J. Sci., 26, 138–44). These acids are readily prepared in pure state and when dried to permanent weight, over sulphuric acid, are used for standardization of alkali V.S. with phenolphthalein or cochineal indicator.

of a reagent may be established by testing for possible impurities it may contain, or by preparing a standard solution of it by titrating it with another standard V.S. If found impure the reagent should be recrystallized or otherwise purified and again titrated.

Preparation of Pure Sodium Carbonate (Na_2CO_3).—Dissolve 300 Gm. of sodium carbonate, C.P. variety, in 250 Cc. of distilled water at 30° C. and filter quickly into a 2-liter flask. Fill the flask with CO_2, then close with a perforated rubber stopper through which pass CO_2 into the solution to saturation, or during one half to three fourth hours. ($Na_2CO_3 + HOH + CO_2 = 2NaHCO_3$). Cool to 0° C. passing CO_2, filter off the crystals through a porous plate and drain by suction. Wash the crystals back into the flask with 50 Cc. of cold distilled water and, keeping up the current of CO_2, filter as before. Repeat this process of washing until 3 Gm. of the purified bicarbonate, dissolved in distilled water, give no reaction for chlorides and sulphates. Dry the product on water-bath and keep in a glass-stoppered bottle. For titration a suitable portion is dried at 270–300° C. by ignition converted into Na_2CO_3 which is then accurately weighed.

Preparation of Pure Potassium Bitartrate ($KHC_4H_4O_6$).— Heat on water-bath during three hours 100 Gm. of the medicinal potassium bitartrate, 85 Cc. of water and 25 Cc. of 10 per cent. hydrochloric acid in a covered beaker, stirring occasionally. Cool rapidly, decant off the solution, wash the residue first by decantation with 100 Cc. of cold water, repeat this and transfer to a plain filter for complete washing. Continue washing the precipitate until a portion of the washings, acidified with HNO_3, gives no reaction with silver nitrate solution. Boil the hydrochloric acid-free salt with just enough hot water to dissolve it (ab. 1500 Cc.), filter and, while cooling, stir the filtrate rapidly until cold. Filter, wash the precipitate with 300 Cc. of cold water run through it in portions, let drain and dry in an air oven at 120° C., to constant weight. Keep the product in a dry, well closed bottle.

Preparation of Pure Oxalic Acid ($H_2C_2O_4 + 2H_2O$).—*A.* Dissolve the acid in cold water, filter and evaporate to three fourths of the volume. Allow to stand to deposit any K or Ca salt. Decant the clear solution, evaporate on water-bath to concentration and stir while cooling to obtain granular crystals. Drain the crystals in a funnel by suction, redissolve in distilled water, concentrate the solution and again crystallize by cooling and stirring. After draining, spread the crystals on several thicknesses of filter paper or blotting paper and dry them, exposed to the air, for several days but keeping them well protected from dust. Keep in well-stoppered bottle.

B. Dissolve the acid in an equal quantity of pure, diluted hydrochloric acid (1.075) by boiling, filter hot if necessary, and cool the clear solution rapidly on ice. Repeat this treatment with the crystals obtained. The second crop of crystals is washed with cold water, recrystallized from hot aqueous solution and dried as given above.

The purified acid should be tested. A solution of 2 Gm. in water

should give no turbidity with silver nitrate; 5 Gm. ignited in platinum should leave no weighable residue on ignition.

C. (*Method of Schmatolla.*) Dissolve 50 Gm. of oxalic acid in 120 Cc. of absolute alcohol, let the solution become cool and filter. To the filtrate add 2 to 3 drops of sulphuric acid (1 + 2), shake the mixture vigorously and let stand twelve hours. Decant the supernatant liquid from any alkali sulphate deposited, distill off the alcohol and dissolve the oxalic acid residue in 200 to 300 Cc. of water. After the solution has stood several hours, filter through a moist filter paper and concentrate filtrate to crystallization. Dry the crystals first at 35–40° C., then in a desiccator over calcium chloride. Keep the product in a dry, well-stoppered bottle.

Standard Volumetric Solutions of the Alkalies.

Normal Potassium Hydroxide V.S.

1000 Cc. contain 56.11 Gm. of KOH.

Preparation and Standardization.—A stronger than $\frac{N}{1}$ solution is prepared by dissolving 75–80 Gm. of pure, stick potassium hydroxide (caustic potash) in water, diluting the solution to about 1100 Cc. and cooling to standard temperature.

Standardization with Potassium Bitartrate.—Of the purified, dry salt (see p. 43) 9.4075 Gm. are dissolved in 160 Cc. of hot distilled water by boiling in a 300-Cc. flask and after 2 to 5 drops of phenolphthalein have been added the hot solution is titrated with the KOH solution. The alkali solution is added to the titrated liquid, slowly, from a burette. When the end-reaction has been approached, the liquid is boiled repeatedly after each addition of a small quantity of the alkali solution, so long as the red color produced by it continues to disappear. End-point of the reaction is indicated when one drop of the V.S. produces a distinct red color, permanent on boiling. For the purpose of checking the first, a second or, if need be, a third titration is then performed, in like manner, and from the average of volumes of the alkali solution consumed in each, if these agree closely, the volume of water required for dilution to normal strength is calculated. The adjustment of strength to normal is based on the following equation; which represents the reaction involved:

$$\underset{188.15}{KHC_4H_4O_6} \; + \; \underset{56.11}{KOH} \; = \; K_2C_4H_4O_6 \; + \; H_2O.$$

1000 Cc. of KOH contain, by definition, 56.11 Gm. of the absolute reagent; 50 Cc. of KOH contain, therefore, 28.055 Gm. of the absolute reagent.

1000 Cc. of KOH react with 188.15 Gm. of potass. bitartrate; 50 Cc. of KOH therefore react with 9.4075 Gm. of potass. bitartrate.

This quantity, 9.4075 Gm. of bitartrate will, therefore, react with 50 Cc. of normal alkali V.S.

Let us suppose that the average of three titrations, of the same quantity of bitartrate, was found to be 47 Cc. of the alkali solution consumed; then to make the solution equal to normal, exactly 3 Cc. of water must be added, to each 47 Cc. of it, both measured at standard temperature. The normality of the V.S. after dilution should be confirmed by another titration with bitartrate and, if found necessary, a new dilution be made. The object of boiling the solution during titration is to remove CO_2, ordinarily present in alkaline solutions which, being acid toward phenolphthalein, interferes with the end-reaction. However, an alkali free from CO_2, need not be boiled. The standardized V.S. should be kept in bottles closed with rubber stoppers carrying tubes filled with soda-lime (Fig. 25). When an alkaline V.S. is to be longer exposed in a burette, the burette should be closed in the same way.

Standardization with Normal Acid V.S.— Titrate the stronger than $\frac{N}{1}$ V.S. of the alkali without heating, in 25 Cc. portions measured from a burette, using 2 drops of methyl orange. As the end-point, the transition reddish color should be adopted. From the
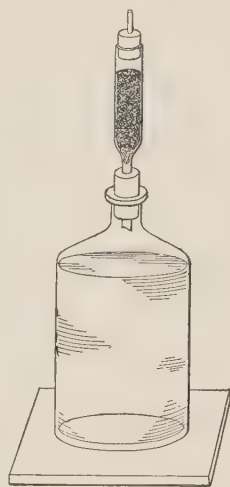
Fig. 25. Container for Standard Alkali V.S.

average of several closely agreeing values calculate the volume of water required for dilution. After diluting, titrate 50 Cc. of the V.S. in the same manner, to confirm the accuracy of the product and, if necessary, make the proper adjustment. Methyl orange is not affected by ordinary quantities of CO_2.

Normal Sodium Hydroxide V.S.

1000 Cc. contain 40.01 Gm. of NaOH.

About 45 Gm. of the pure, stick caustic soda are roughly weighed, the carbonate on the surface washed off with a stream of water free from CO_2, and then dissolved in distilled water to measure 1000 Cc. When the solution has cooled to standard temperature, it may be used for titration of 9.408 Gm. of pure potassium bitartrate or may be standardized by titration with normal acid, the method given for $\frac{N}{1}$ KOH being also applicable to this solution. When standardized, the solution is to be kept in proper containers (Fig. 25). Its uses and keeping are identical with those of potassium hydroxide V.S.

It has been suggested to prepare a strong stock solution of NaOH to be used for the preparation of V.S. of alkalies. A nearly 50 per cent. solution, prepared by dissolving 150 Gm. NaOH in 50 Cc. of water is made. This, on standing, deposits most of the impurities, while the supernatant liquid then siphoned off is free from carbonate. For $\frac{N}{10}$ V.S., 8.5 Gm. $=$ to 5.75 Cc. should be diluted with

distilled water to measure 1000 Cc. and then standardized by titration.

Half-Normal Alkali (KOH or NaOH) V.S.

1000 Cc. contain 28.055 Gm. of KOH,
20.005 Gm. of NaOH.

According to volume of the V.S. desired, a definite volume of the corresponding normal alkali V.S. is diluted with an exactly equal volume of water, both measured at standard temperature. The diluted solution should be checked by titration with $\frac{N}{1}$ acid V.S. using M.O. The standardized solution is then transferred to clean dry bottles in which it is to be kept. The solution should be well protected from dust, moisture and CO_2.

The equivalents of $\frac{N}{2}$ V.S. must necessarily be one half of the corresponding normal values.

Half-normal Alkali, Free from CO_2.—Add a clear, saturated solution of barium hydroxide to the $\frac{N}{2}$ Alkali V.S. until precipitation no longer takes place, mix well, let the precipitate deposit and decant the clear liquid into a clean, dry bottle from which CO_2 has been removed by a current of CO_2-free air. Keep securely closed with a stopper provided with soda-lime protection tube (Fig. 25). When to be transferred to a burette for use, the solution should be preferably drawn in by suction as in the case of $Ba(OH)_2$ V.S. The exact strength of the V.S. should be determined at the time of its employment for titrations.

Fifth-Normal Alkali V.S.

1000 Cc. contain 11.222 Gm. of KOH,
8.002 Gm. of NaOH.

Tenth-Normal Alkali V.S.

1000 Cc. contain 5.611 Gm. of KOH,
4.001 Gm. of NaOH.

Fifth and tenth normal V.S. of alkalies are prepared from the stronger standard V.S. by proper dilution and subsequent checking as in the case of the $\frac{N}{2}$ V.S. When a large volume of one of these solutions is to be prepared, direct standardization with potassium bitartrate or with normal acid is to be made, following the method given for the standardization of the normal alkali V.S. Of the bitartrate 0.1 of the quantity there given (0.9408 Gm.) will have to be employed, whereas each cubic centimeter of the normal V.S. will correspond to 10 Cc. of the $\frac{N}{10}$ V.S. For the $\frac{N}{10}$ V.S. the solution prepared for standardization should contain about 8 Gm. of KOH or 6 Gm. of NaOH to the liter. After titration the stronger solution is diluted so that 50 Cc. of it will exactly neutralize 0.9408 Gm. of bitartrate or 5 Cc. of the normal acid V.S. The equivalents of the fifth-normal are one fifth, and of the tenth-normal one tenth of the values of the corresponding normal equivalents.

Twenty-fifth-Normal Alkali V.S.

1000 Cc. contain 2.2444 Gm. of KOH, or
1.6004 Gm. of NaOH.

Fiftieth-Normal Alkali V.S.

1000 Cc. contain 1.1222 Gm. of KOH, or
0.8002 Gm. of NaOH.

Hundredth-Normal Alkali V.S.

1000 Cc. contain 0.5611 Gm. of KOH, or
0.4001 Gm. of NaOH.

These V.S. are prepared by dilution of the corresponding stronger standard V.S. and checking the strength of the product. Directions for their keeping are the same as for all the other alkali V.S. The weaker solutions do not keep well and should, therefore, be often renewed.

Tenth-Normal Sodium Carbonate V.S.

1000 Cc. contain 53.00 Gm. of Na_2CO_3.

Dissolve 5.30 Gm. of the pure sodium carbonate (see p. 43), dried at 270 to 300° C., in sufficient distilled water to measure, at standard temperature, exactly 1 liter. Equivalents of this V.S. are identical with those of the tenth-normal alkali V.S.

Tenth-Normal Barium Hydroxide V.S.

1000 Cc. contain 15.7775 Gm. of $Ba(OH)_2 + 8\ H_2O$, or
8.57 Gm. anhydrous $Ba(OH)_2$.

About 20 Gm. of the crystalline base are dissolved in distilled water, the solution diluted to 1100 Cc. in a flask, the flask closed and allowed to stand 2 days to deposit $BaCO_3$. The clear liquid is then transferred by siphoning to a clean bottle from which CO_2 has been removed by a current of CO_2-free air, passed during one half hour. The bottle is then at once closed with a rubber stopper provided with a soda-lime tube (see Fig. 25, p. 45). Several portions of $\frac{N}{10}$ hydrochloric acid (about 25 Cc. accurately measured) are then titrated with this clear solution, using methyl orange. In titration the burette should preferably be joined to the bottle as shown in Fig. 18, or closed with a stopper provided with a soda-lime tube. The average of two or more closely agreeing titrations is then used for calculation of the volume of water required for dilution to $\frac{N}{10}$ strength. If, for example, 23.8 Cc. of the alkaline solution were consumed by 25 Cc. of the $\frac{N}{10}$ acid, then for each 23.8 Cc. of the solution, exactly 1.2 Cc. of water, both being measured at standard temperature, must be supplied to convert the solution into tenth-normal. If the solution is to be used as an empirical V.S., and this is to be preferred on account of the turbidity on dilution and weakening on keeping, then its value in terms of the $\frac{N}{10}$ V.S. is found:

$$23.8 : 25 :: 100 : x.$$

$$x = \frac{25 \times 100}{23.8} = 105.042 \text{ per cent.}$$

The strength of the empirical V.S. is, therefore, 105.042 per cent. of the tenth-normal, and one Cc. $= 1.05042$ Cc. of $\frac{N}{10}$ V.S. If this factor is to be used, it should be properly recorded; however, the actual quantity of $Ba(OH)_2$, in one Cc., may be calculated and equivalents based on it.

For barium hydroxide V.S. two advantages are claimed, namely: it attacks glass less readily than the alkalies and holds no CO_2 in solution; any carbon dioxide absorbed by it forms $BaCO_3$ which precipitates. This, of course, makes the solutions weaker on this account and necessitates frequent restandardization.

Empirical Alcoholic KOH V.S. $\left(\text{nearly } \frac{N}{2}\right)$.

KOH $= 56.11$.

The empirical solution is made by dissolving 30 Gm. of potassium hydroxide, purified by alcohol, in 1000 Cc. of 95 per cent. alcohol, heating the alkali with alcohol under a return condenser. After standing 24 hours the solution is filtered into a clean, dry bottle in which it is kept, properly protected from dust and CO_2, in a cool place. The solution thus prepared readily becomes colored from yellow or red-brown and changed in strength on keeping; it must, therefore, be often restandardized, preferably at the time of its employment in determinations. The exact strength of the V.S. is established by titrating with it 20 Cc. portions of $\frac{N}{2}$ hydrochloric acid V.S., using methyl orange. From the results of titration the factor (equivalent of 1 Cc. of the V.S.) is calculated and employed, or the value of the solution is expressed, as percentage of the $\frac{N}{2}$ V.S. Further, the equivalent volume of the solution, e. g., the volume of it corresponding to 1 Cc. of $\frac{N}{2}$ V.S. may be found, and when a definite quantity of $\frac{N}{2}$ alcoholic KOH is called for, the corresponding volume of the empirical solution can be taken.

Note: To keep the solution colorless, preparation at room temperature and exposure to diffused daylight have been recommended by Halla. Light is supposed to destroy any yellow color. The solution will remain colorless much longer if prepared from alcohol which has been boiled during 1 hour with some KOH under return condenser and then distilled.

Stable alcoholic KOH can be prepared from potassium sulphate and barium hydroxide. The sulphate is used in $\frac{N}{2}$ V.S. and the hydroxide in N-V.S., sufficient of each being taken to supply the equivalents required for reaction as shown by the equation:

$$K_2SO_4 + Ba(OH)_2 = BaSO_4 + 2KOH.$$
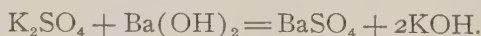
To the mixture is added alcohol to amount to 80 per cent. Excess

of $Ba(OH)_2$ is precipitated by a little strong solution of K_2SO_4. The clear alkali is then siphoned into a clean bottle for use.

The employment of 10N KOH in water to be mixed with 95 per cent., or absolute alcohol, is recommended by Siegfeld (Chem. Zeit., 32, 63–4). For standardization the 10N KOH is weighed into a flask, alcohol added to it and the alcoholic solution, after heating for 15 minutes under return condenser, titrated with $\frac{N}{2}$ or $\frac{N}{10}$ HCl V.S.

Standard Volumetric Solutions of Acids.

Normal Hydrochloric Acid V.S.

1000 Cc. contain 36.47 Gm. of HCl.

Preparation and Standardization.—A somewhat stronger than normal solution of the acid is prepared by adding to 130 Gm. of pure, strong hydrochloric acid (1.16), or 110 Cc. of (1.20), sufficient water to measure 1000 Cc.

Standardization with Normal Alkali V.S.—For titration, 20 Cc. of the acid at standard temperature are carefully measured from a burette into a titration flask, diluted to 50 Cc. with distilled water, 2 drops of methyl orange added and the solution titrated with recently standardized normal KOH or NaOH V.S. The addition of the alkali V.S. should be gradual, the flow being reduced to drops towards the end of the operation. The titration is completed when the transition rose tint is changed by one drop of the V.S. to distinct yellow color, permanent on shaking. After reading the burette, a second titration should be made of another 20 Cc. portion of the acid for a check and, if the results do not agree closely, a third titration will be necessary. From the average of several agreeing results the volume of water required for dilution of the acid is found. The acid is then diluted to normal strength, the difference between the average of the readings and 20, representing the Cc. of water to be added to each 20 Cc. of it. For instance, if 20 Cc. of the acid required an average of 21.5 Cc. of the N alkali V.S. for neutralization, then by diluting 20 Cc. of the acid to 21.5 Cc., the acid will be made of equal value with the alkali or will become normal. Therefore, for every 20 Cc. of the acid, exactly 1.5 Cc. of water must be added, standard temperature being observed in measuring. After proper dilution the correspondence of the two solutions should be confirmed by a titration in which 50 Cc. of the acid are employed. Should the acid be found still stronger than normal another dilution must be made. Should, after dilution, the acid be found weaker than normal, the required volume of the stronger solution may be added, or, if that is not on hand, the solution is made stronger than normal by the addition of a little of the concentrated HCl, and the process of standardization repeated. The weaker solution can, however, be employed as an empirical V.S.

Standardization with Sodium Carbonate.—About 8 to 10 Gm. of pure sodium bicarbonate, prepared as directed under preparation of sodium carbonate (p. 43), are placed in a platinum crucible or dish and dried at 80–90° C. The crucible and contents are then

5

transferred to a sand-bath or perforated asbestos plate and heated
at 270–300° C. during one half to one hour. The sodium carbonate
must be completely exsiccated, but should not fuse. After cooling
in a desiccator, the crucible and contents are weighed, and heating,
cooling and weighing, is repeated until the weight is constant. The
cold carbonate is then transferred to a clean, dry, tared weighing
bottle. For one titration, about 2 Gm. of the salt are accurately
weighed, by difference, into a 200 Cc. erlenmeyer flask, dissolved
in 100 Cc. of distilled water, 3–5 drops M.O. added and the solu-
tion titrated with the stronger hydrochloric acid solution. During
titration the titrated liquid should be kept well mixed, and the flow
of the V.S. reduced to drops toward the end of the operation, the
approach of which is indicated by rapid temporary changes of color.
Titration should be suspended as soon as the solution takes on a
transition (orange) color. At this point the burette is read and
the reading accepted if one drop of the V.S., subsequently added,
gives a distinct red color. Otherwise more HCl should be dropped
in until the desired end-reaction is obtained. To check the accuracy
of the first titration another or several such should be performed in
precisely the manner of the first; their agreement should be close.

To calculate the strength of the acid and adjust it to the normal
value, let us suppose that 1.984 Gm. of dry sodium carbonate were
taken and the solution of the HCl required to neutralize this meas-
ured 36 Cc., this being an average of three titrations. Then, from
an equation, representing the reaction in question:

$$\underset{106.00}{Na_2CO_3} + \underset{2 \times 36.47}{2HCl} = 2NaCl + CO_2 + H_2O.$$
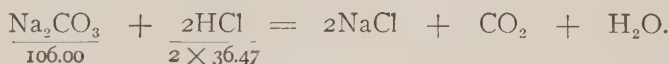
It is seen that 106.00 Gm. of pure sodium carbonate react with
2 × 36.47 Gm. of absolute HCl, or that 53.0 of the former react
with 36.47 Gm. of the acid. The equivalent of 36.47 Gm. of HCl,
or of 8 Gm. of oxygen is, therefore, 53.0 Gm. of sodium carbonate.
But 36.47 Gm. is the quantity of HCl which must be present in
1000 Cc. of its normal V. solution. The question that now arises is:
What volume of N hydrochloric acid will be required to neutralize
the 1.984 Gm. of sodium carbonate used in the titration? By
proportion:

$$53.0 : 1000 :: 1.984 : x.$$

$$x = \frac{1000 \times 1.984}{53.0} = 37.43 \text{ Cc.}$$

This is found to be 37.43 Cc. It is at once evident that the acid
is stronger than normal, 36 Cc. instead of 37.43 Cc. having been
used to neutralize the carbonate. To dilute the acid to normal
strength, 1.43 Cc. of water must, therefore, be added to every 36
Cc. of it, measuring the liquids at standard temperature. If 950
Cc. of the acid were to be so diluted, the volume of water required
would be:

$$36 : 1.43 :: 950 : x.$$

$$x = 37.73 \text{ Cc.}$$

To confirm the normality of the acid after dilution, another titration should be performed, and the proper adjustment made if necessary.

Standardization by Direct Weighing of the Acid.—An accurately calibrated 100 Cc.-flask, provided with a rubber stopper having two perforations through one of which a fine capillary tube extends to the bottom of the flask while into the other is inserted a short piece of glass tubing, is accurately weighed together with about 90 Cc. of distilled water. A slow stream of pure, dry HCl, generated from $NH_4Cl + H_2SO_4$ and washed through sulphuric acid, then calcium chloride, is passed into the water until somewhat more than the gramme-equivalent weight has been absorbed. This is found by occasional rough weighing. The gas is then discontinued, the solution allowed to cool and the flask and contents are accurately weighed. The increase in weight is the quantity of HCl added. From this the volume of water required to be added to make the acid normal, is calculated. The acid in the flask is made up to the mark at standard temperature and the water required for dilution is then added from a burette. If, for example, 3.84 Gm. of HCl has been dissolved, the quantity of HCl in its normal solution being 3.647 Gm. in 100 Cc., then:

$$3.647 : 100 :: 3.84 : x.$$

$$x = 105.3.$$

That is, 105.3 Cc. of a normal V.S. of the acid contain 3.84 Gm. of HCl. Since this quantity of HCl is present in 100 Cc., 5.3 Cc. of water must be added. The dilution having been properly made at standard temperature, the standard acid is then transferred to a dry glass-stoppered bottle and kept in a cool place and away from direct sunlight.

The volume of the acid thus prepared is rather small and would be mainly useful for standardization of the alkali V.S., and through these, other acids. However, a large volume of standard HCl may be prepared in this manner when an accurate balance of the necessary capacity is available. This method of standardization is also applicable to the preparation of standard sulphurous acid V.S. for iodometry.

Other Methods.—1. Gravimetrically, hydrochloric acid may be standardized by precipitation with silver nitrate and calculation of the quantity of HCl present in a given volume of the acid from the quantity of silver chloride produced. Though this is a very accurate method of determination of chlorides, it can not be considered reliable for the purpose of establishing an exact volumetric standard. This will be apparent in view of the following considerations: The gravimetric method differs in technique, employs different set of measuring instruments and determines a different ion (Cl^-) than the one (H^+) of value for purposes of titration; besides not utilizing an end-reaction and requiring no indicator, it is independent of those factors which are important to the volumetric method.

2. The strength of normal hydrochloric acid V.S. may also be determined and checked with pure sodium bicarbonate (see method

of preparation, p. 43). About 2 Gm. of the salt are placed in a tared platinum dish, dissolved in a minimum volume of water, a drop of M.O. added and the HCl V.S. added from a burette until the yellow color is changed to distinctly red. The solution is then evaporated to dryness, the residue dried and gently ignited to constant weight. From the quantity of NaCl obtained, and the volume of HCl solution added, the strength of the acid is calculated.

$$HCl + NaHCO_3 = NaCl + H_2O + CO_2.$$

Normal Sulphuric Acid V.S.

1000 Cc. contain 49.045 Gm. of H_2SO_4.

To prepare a stronger than normal solution of the acid, 30 Cc. of the concentrated acid, Sp.Gr., 1.83 at 20° C., are added to 1020 Cc. of water. When the solution has cooled to standard temperature, it is standardized by titration with N alkali V.S., or, pure sodium carbonate is titrated with it, just as in the case of hydrochloric acid standardization, q.v. The solution is then diluted to N strength and checked by another titration.

Gravimetrically, sulphuric acid solution is standardized by precipitating the acid present in a definite volume of stronger than N solution as barium sulphate with $BaCl_2$ in excess, heating until the precipitate settles completely, filtering, washing, drying, and finally igniting. From the weight of $BaSO_4$ obtained, the amount of absolute H_2SO_4 in the solution is found by calculation. The acid, if stronger than normal, is then properly diluted. On the value of this method of standardization the same comment may be made as on the gravimetric method for HCl. (See p. 51.)

The strength of sulphuric acid solutions may be determined or checked with bicarbonate, as in the case of HCl (see p. 51). The alkali sulphates are less volatile than the chlorides, and the residue may therefore be ignited without loss.

Half-Normal Acid V.S.

1000 Cc. contain 18.235 Gm. of HCl, or
24.5225 Gm. of H_2SO_4.

These V.S. are prepared by dilution of the stronger standard acids with an exactly equal volume of water, measured at standard temperature. After dilution, the strength of the product is checked by titration and any adjustment required is made.

The equivalents of these acids are one half of the values of the corresponding normal acids.

Fifth-Normal Acid V.S.

1000 Cc. contain 7.294 Gm. of HCl, or
9.809 Gm. of H_2SO_4.

Tenth-Normal Acid V.S.

**1000 Cc. contain 4.9045 Gm. of H_2SO_4, or
3.647 Gm. of HCl.**

Fifth-normal acid is prepared by dilution and checking with a standard alkali V.S. The tenth-normal V.S. is prepared in the same manner, but as it is often used in large volumes, it is better to standardize it directly with sodium carbonate or with N alkali V.S. The method of standardization of tenth-normal acid is the same as for the normal solution, one tenth of the quantities there required being employed.

The equivalents of the $\frac{N}{5}$ V.S. are one fifth, and those of the $\frac{N}{10}$ are one tenth of those of the normal solutions, p. 89.

The alkaloidal equivalents are given on p. 90.

Twenty-fifth-Normal Acid V.S.

**1000 Cc. contain 1.458 Gm. of HCl, or
1.9618 Gm. of H_2SO_4.**

Fiftieth-Normal Acid V.S.

**1000 Cc. contain 0.7294 Gm. of HCl, or
0.9809 Gm. of H_2SO_4.**

Hundredth-Normal Acid V.S.

**1000 Cc. contain 0.49045 Gm. of HCl, or
0.3647 Gm. of H_2SO_4.**

These acids contain the indicated fractions of the reagents present in normal solutions. They are prepared by proper dilution of the corresponding standard V.S. of greater strength.

Tenth-Normal Oxalic Acid V.S.

1000 Cc. contain 6.303 Gm. of $H_2C_2O_4 + 2H_2O$.

If an absolutely pure acid be had, such as the sublimed oxalic acid (Merck), the quantity of it required to make $\frac{N}{10}$ V.S. can be dissolved in water and the solution used. But the acid, even the purified kind, being apt to vary in composition, mainly on account of the variability of its water of crystallization, it is necessary to prepare a stronger than $\frac{N}{10}$ solution and standardize it with a tenth-normal alkali V.S. which has been recently standardized. By dissolving 6.4 Gm. of the purified acid (see p. 43) in water, to measure 1000 Cc., such solution is obtained.

Of the $\frac{N}{10}$ alkali, 20 Cc. are accurately measured into a flask, 30 Cc. of water added and the solution heated to boiling. The hot solution is titrated, with the oxalic acid run in from a burette, in the presence of 2 drops of phenolphthalein. When the pink color of the titrated liquid has been just discharged by one drop of the oxalic acid, the solution is boiled to remove any CO_2 present, and the red color will, when the gas has escaped, be restored. Oxalic acid should now be added, drop by drop, and as soon as the solution is

decolorized, boiling should be repeated until the pink color no longer appears on boiling. The titration should be repeated with more 20 Cc. portions of the alkali V.S., and the average value of the closely agreeing ones should be taken for calculation of the water required. After the dilution has been made the solution should be checked with 50 Cc. of the $\frac{N}{10}$ alkali V.S. and, if need be, another adjustment made.

If, for example, 20 Cc. of $\frac{N}{10}$ alkali V.S. required 18.2 Cc. of the acid, this being the average of several titrations, to dilute the acid to the $\frac{N}{10}$ strength, it is seen that 1.8 Cc. of water are needed for every 18.2 Cc. of the oxalic acid. The solution of the acid and the water to be added are, of course, accurately measured at standard temperature.

Tenth-normal oxalic acid is chiefly employed in the oxidation analyses, in conjunction with potassium permanganate V.S. See Chapter III.

A. ALKALIMETRY.

Alkalimetry comprises determinations of bases, by titration, with standard acid V.S. The soluble bases are titrated directly; for the insoluble, or sparingly soluble ones, residual titration is employed.

I. The Inorganic Bases.

Soluble Bases.

1. Determination of Soluble Hydroxides.

Potassium hydroxide, sodium hydroxide and ammonium hydroxide.

Volumetric solution: Normal or half-normal acid (sulphuric acid preferred).

Indicator: Methyl orange.

Accurately weigh a suitable quantity of the sample (2 to 5 Gm. of solid, 10 to 50 Gm. of solution),[1] dissolve the solid and dilute the solution in either case to measure a definite volume, 50 to 100 Cc., at standard temperature. By means of a pipette or from a burette, measure aliquots of 10 to 20 Cc. into several titration flasks, dilute each portion to measure 50 Cc., add 2 drops of the indicator and titrate with the standard acid V.S. Add the V.S. to the solution of the sample in small portions, mixing well after each addition, and reducing the flow to drops toward the end of the operation, the approach of which is made evident by the change of yellow to a reddish color. Read the burette after some time has been allowed for complete draining and accept the reading only if a drop of the V.S. then added is found to change the transition color to pure light red. Otherwise, more of the V.S. should be added, drop by drop, until the end-reaction is obtained. Titrate the other portions in this manner, and from the average of at least two closely agreeing readings, calculate the percentage of the particular hydroxide in the sample. For calculation, apply rule given on p. 24.

[1] The quantity of the sample for one titration with any V.S. should be so approximated as to require from 20 to 40 Cc. of the V.S. See also p. 23.

Illustration.—Four grammes of caustic soda, dissolved in water, to measure exactly 40 Cc., and titrated in 10 Cc. portions required: 20.2 Cc., 20.0 Cc., 20.1 Cc. of normal acid respectively; to calculate percentage of NaOH in the sample.

The factor (equivalent of 1 Cc. of N-acid) for NaOH is 0.04001 Gm. (see table, p. 89) and is derived from the equation:

$$\underset{40.01}{\text{NaOH}} \; + \; \underset{36.47}{\text{HCl}} \; = \; \text{NaCl} \; + \; \text{H}_2\text{O}.$$

36.47 parts of HCl react with, or neutralize, 40.01 parts of NaOH.

1 Lt. of N-HCl contains 36.47 Gm. and neutralizes, as seen in the equation 40.01 Gm. of NaOH. Since 36.47 Gm. of HCl $=$ 40.01 Gm. of NaOH, then 1 Cc. of the N-acid is the equivalent of $\frac{40.01}{1000}$ Gm. of NaOH.

The factor is therefore found to be 0.04001 Gm.

Now, as 20.1 Cc. was the average of V.S. required to neutralize 10 Cc. of the solution of the sample containing 1 Gm.,

20.1 $\times$ 0.04001 $=$ 0.8042 Gm. of NaOH in 1 Gm. of the sample, and the proportion:

$$1.0 : 0.8042 :: 100 : x, \text{ will give the percentage.}$$

$$x = \frac{0.8042 \times 100}{1.0} = 80.42,$$

hence the sample is found to contain 80.42 per cent. of NaOH.

Observations.—The other hydroxides are determined in the same way, care being taken to employ the proper factors in calculations. With V.S. of other strengths, viz.: the half-, fifth-, tenth-normal, etc., the volume of the volumetric solution consumed in titration may be converted into the normal, in which case the normal factors are used, or, their own factors are derived from the normal equivalents. It will also be seen that the *equivalents of 1 Cc. of normal V.S. constitute the equivalents of 2 Cc. of half-normal*, 5 Cc. of fifth-normal or 10 Cc. of tenth-normal V.S., etc.

With the empirical V.S., whose strength is expressed in per cent. of the nearest normal V.S., the calculation remains the same, the resulting value being finally multiplied by the factor of the empirical V.S. used. However, if the strength of such solutions is expressed in quantity of any particular base, the empirical V.S. can be used for other bases only after its value, in terms of the base determined, has been calculated.

Soluble hydroxides absorb CO_2 readily and when titrated with M.O. both the hydroxide and carbonate are indicated. To find only the hydroxide present, phenolphthalein would have to be used, the end-reaction being reached when one half of the carbonate has been decomposed. (See titration of hydroxides and carbonates together.) Solutions of calcium hydroxide and barium hydroxide are titrated, just as other hydroxides, with phenolphthalein as indicator, standard HCl being employed.

2. DETERMINATION OF AMMONIA IN AMMONIUM SALTS.

Ammonium salts are decomposed when heated in solution with certain bases. The NH_3 given off is distilled into an excess of standard acid and from the volume of the acid neutralized, the quantity of ammonia is calculated.

Apparatus for Distillation.—The ammonia-distilling apparatus, one form of which is represented in Fig. 26, consists of two flasks;
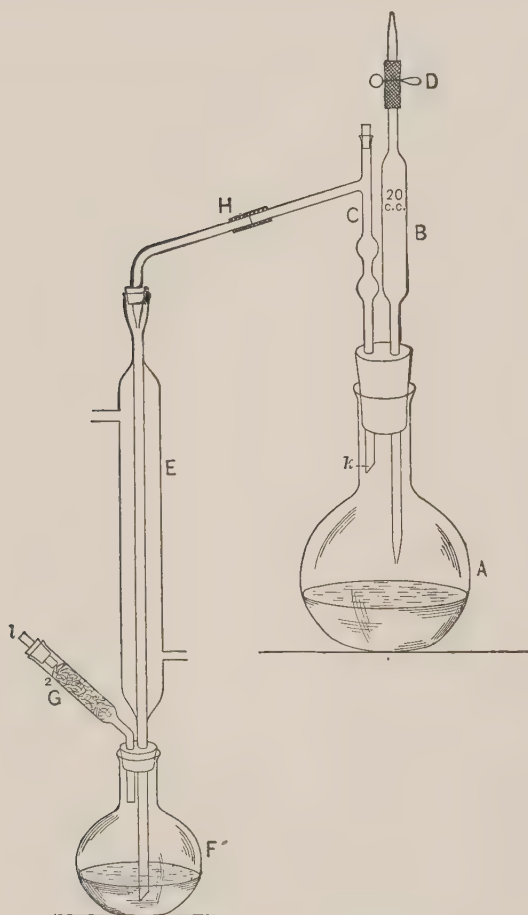
FIG. 26.   AMMONIA-DISTILLING APPARATUS.

the large flask *A* is of 500 Cc. capacity, the smaller one *F* holding about 250 Cc., both being preferably of the erlenmeyer form; a Liebig condenser *E*, body 2 ft.; bulbed adapter *C*, best 3-bulbed, with obliquely ground stem *k*; a pipette *B*, closed with rubber tubing and a pinchcock and a guard tube *G*, which contains glass wool and has a perforated stopper carrying a short tube *l*. In the larger flask

the sample is decomposed by heating it in solution with the base, the solution of which is introduced through the pipette. When more than a pipetteful of the alkali is needed, a small funnel is attached to the upper end of the pipette and the alkali solution poured in through it. The bulbed adapter condenses some of the water vapor but serves chiefly to retain any alkali which may be carried up by foaming, or be thrown up by bumping of the alkaline liquid on boiling. In the condenser most of the ammonia is dissolved in the water collecting there by condensation and is delivered into the smaller flask serving as a receiver. The receiver contains the standard acid V.S. with a portion of which the glass wool in the guard tube is moistened. These parts of the apparatus are connected as shown in the figure, the pipette and the stem of the adapter pass through a rubber stopper closing the large flask, and the adapter is joined to the condenser by the bent tube H. The lower end of the condenser should extend about one fourth inch below the surface of the acid in the receiver.

Reagents Needed.—Solution of NaOH or KOH, 10 per cent., recently boiled, or ignited MgO.

Half-normal acid V.S.

Half-normal alkali V.S.

Litmus solution.

Methyl orange.

Ammonia-free water.

Paraffin, about 1 Gm.

Procedure.—Into the decomposition flask A, introduce 0.5 to 1.0 Gm. of the sample accurately weighed, or a measured volume of a solution containing nearly an equal quantity, cover with 50 Cc. of ammonia-free water, add some of the litmus solution and drop in a piece of paraffin. Into the receiver flask F, measure from a burette 30 to 50 Cc. of half-normal acid V.S. (volume of the acid is based on the proportion of 50 Cc. acid to 1 Gm. sample) and dilute with an equal volume of water, then, by means of a small pipette, transfer some of the acid to the guard tube to moisten the glass wool with it, the pipette being washed out into the receiver. Fill pipette B with the strong, boiled alkali solution, connect the apparatus and, having introduced sufficient of the alkali to impart to the liquid in the flask a distinctly alkaline reaction, add 5 Cc. more for excess, and start the distillation by heating flask A. Distill at gentle boiling during twenty minutes, or until the liquid in the receiver is nearly doubled. To discontinue, remove the flame only after the apparatus has been disconnected. Raise the condenser, wash out the inner tube washing off the outside of the lower end at the same time into the receiver. Then wash the acid of the guard tube into the receiver by allowing some water to percolate through the tube. Having added the indicator, titrate with the half-normal alkali V.S. as in the titration of acids. The alkali V.S. is added until the red color of the titrated liquid becomes changed to a distinct yellow tint by one drop of the V.S. From the volume of the half-normal acid consumed by the ammonia, which constitutes the difference between the volume of standard acid

originally taken, and the volume of the standard alkali required for the acid unconsumed by NH_3, calculate the percentage of ammonia in the sample. To confirm the results of the determination another distillation and titration should be made.

Illustration.—The ammonia distilled from 1 Gm. of a sample of ammonium salt was passed into 50 Cc. of half-normal acid and the unconsumed acid required 22.4 Cc. of half-normal alkali V.S. for neutralization. In the subsequent titration, in which identical quantities were employed, the acid required 22.6 Cc. of half-normal alkali V.S.; to calculate the percentage of ammonia in the sample.

The average of alkali V.S. in the two titrations is 22.5 Cc.

The volume of half-normal acid consumed by NH_3, 50 — 22.5 = 27.5 Cc.

The factor for ammonia (equivalent of 1 Cc. $\frac{N}{2}$ acid) is 0.00852 Gm. and is derived from the equation:

$$\underset{98.09}{H_2SO_4} \ + \ \underset{2 \times 17.04}{2NH_3} \ = \ (NH_4)_2SO_4.$$

1 Lt. of $\frac{N}{2}$ H_2SO_4 contains 24.523 Gm. and corresponds to 8.52 Gm. of NH_3.

1 Cc. of $\frac{N}{2}$ H_2SO_4 contains 0.024523 Gm. and corresponds to 0.00852 Gm. of NH_3.

The factor is, therefore, 0.00852 Gm.

27.5 × 0.00852 = 0.2343 Gm. of ammonia in 1 Gm. of the sample. By proportion:

$$1.0 : 0.2343 :: 100 : x.$$

$$x = \frac{0.2343 \times 100}{1.0} = 23.43 \text{ per cent. of ammonia in the sample.}$$

To express the result as ammonium (NH_4) or as nitrogen (N), the desired values are found by proportion:

For ammonium: $17.04 : 18.05 :: 23.43 : x.$
For nitrogen: $\quad 17.04 : 14.01 :: 23.43 : x.$

However, it is better to employ, in calculation, the proper factors corresponding to NH_4 and nitrogen at once as in the case of NH_3.

Observations.—During the distillation the vapors in the larger flask will condense and diminish the pressure on the acid in the receiver; the apparatus being connected air tight, the acid is found rising in the condenser. Should heating be interrupted through any cause there is danger of the acid being drawn over into the decomposition flask and causing loss of the analysis. It is for this reason necessary to keep the lower end of the condenser just immersed in the V.S. in the receiver, under which conditions the passing of the acid into the retort is impossible.

Bumping of the boiling liquid may be prevented by placing, in the solution, pieces of pumice stone, of broken glass, or a spiral of platinum wire. To overcome the rising of foam a small quantity of

paraffin is added to the contents before distillation has commenced.

Magnesium oxide is recommended and used for liberation of ammonia from its salts when other nitrogen compounds are present. The oxide, which should be free from carbonate and from ammonium compounds is added to the cold solution of the sample to be distilled. About 5–10 Gm. should be used for 0.5 to 1 Gm. of the sample, and the distillation be allowed to proceed 4 to 5 times as long as with NaOH. It has, however, been stated that MgO is not a suitable agent for this purpose in presence of a large quantity of chlorides, additional evidence being presented by P. A. Kober (J. A. Chem. Soc., 1908, 30, p. 1270), who ascribes the retention of NH_3 to the reversible reaction:

$$MgCl_2 + NH_4OH \rightleftarrows Mg(OH)_2 + 2NH_4Cl.$$

Nitrates and nitrites may both be determined by the distillation method. They are reduced in solution by nascent hydrogen and the ammonia produced is titrated after being distilled into standard acid.

Nitrogen, in organic compounds, when determined by the Kjeldahl method, is converted into ammonia by pyrosulphuric acid. The ammonia in the ammonium sulphate formed is then determined by distillation, calculated into N and, from the quantity of this found, the percentage of the proteid or other organic compound is calculated.

3. Determination of Soluble Carbonates and Bicarbonates.

Carbonates and bicarbonates of sodium and potassium.

Volumetric solution employed: $\frac{N}{2}$, or N acid.

Indicator: Methyl orange or phenolphthalein.

The titration in the determination of these compounds, using M.O., is carried out just as in the case of the hydroxides. If weaker volumetric solutions be used, the CO_2 would be objectionable and should then be removed. When a pink color has been produced by the acid V.S. the titrated liquid is boiled; after cooling more M.O. is added and the titration completed. For each titration about 2 Gm. for a N solution or 1 Gm. for $\frac{N}{2}$ V.S. should be taken. With methyl orange the reaction is completed according to the following equation:

$$a. \quad \underset{106}{Na_2CO_3} + \underset{98.09}{H_2SO_4} = Na_2SO_4 + CO_2 + H_2O.$$
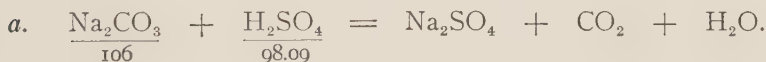
98.09 parts of sulphuric acid react with 106.00 parts of Na_2CO_3. Since 1 Lt. of $N-H_2SO_4$ V.S. contains 49.045 Gm., and corresponds to 53.0 Gm. Na_2CO_3,

1 Cc. of the V.S. is the equivalent of 0.0530 Gm. of anhydrous sodium carbonate.

1 Cc. of the V.S. is the equivalent of 0.06201 Gm. of monohydrated sodium carbonate, etc., using methyl orange.

With phenolphthalein same reaction is obtained only by boiling the

titrated solution; in the cold the end-reaction takes place when the carbonate is all converted into bicarbonate, as represented:

b. $2Na_2CO_3$ $+$ H_2SO_4 $=$ Na_2SO_4 $+$ $2NaHCO_3$.
$$\underset{2 \times 106}{} \qquad \underset{98.09}{}$$
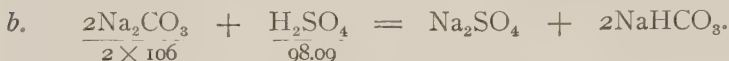
Only one half of the carbonate is thus indicated.

98.09 parts of H_2SO_4 react with 2×106 parts of Na_2CO_3. Since 1 Lt. of $N\text{-}H_2SO_4$ V.S. contains 49.045 Gm., and corresponds to 106 Gm. of Na_2CO_3,

1 Cc. of the V.S. is the equivalent of 0.106 Gm. of anhydrous sodium carbonate.

1 Cc. of the V.S. is the equivalent of 0.12402 Gm. of monohydrated sodium carbonate, etc., using phenolphthalein.

In deriving the factors for carbonates and bicarbonates titrated with phenolphthalein as indicator, care must be exercised not to overlook whether the titration was in cold or boiling solution.

4. Determination of Ammonium Carbonate.
(Residual Titration.)

Volumetric solutions employed: Normal or $\frac{N}{2}$ H_2SO_4, and N, or $\frac{N}{2}$ alkali.

Indicator: Litmus solution.

To an aliquot portion of the solution of a sample prepared as given under hydroxides, add an excess of normal sulphuric acid V.S., measuring accurately, boil gently to remove CO_2, allow to cool, add litmus solution to color, and titrate the unconsumed acid with normal or $\frac{N}{2}$ alkali V.S. When the V.S. has changed the red color of the titrated liquid to violet which is then changed by one drop of it to distinct blue, the titration is ended. Subtract from the volume of the N acid V.S. added, the volume of normal alkali or half the volume of $\frac{N}{2}$ V.S. and from the difference constituting the volume of acid consumed by the sample used, calculate the percentage of ammonium carbonate present.

1 Cc. of N acid V.S. is the equivalent of 0.052346 Gm. of ammonium carbonate, U. S. P.

5. Determination of the Organic Salts of the Alkalies.

Organic salts of the alkalies are, by carbonization and ignition, converted into corresponding carbonates which are then titrated.

Volumetric solution employed: Normal or $\frac{N}{2}$ acid V.S.

Indicator: Methyl orange.

Weigh accurately, into a porcelain crucible, about 2 Gm. of the sample and ignite it, keeping the crucible covered. Apply heat slowly at first and very gradually increase it to dull redness. When carbonization is completed (no volatile products escape) cool the crucible and extract the residue with two successive portions of hot water, decanting the solution through a small filter paper into the titration flask. Transfer the insoluble matter to the filter and wash with hot water until last portions of the washings no longer react

with the acid methyl orange test paper. Combine the filtrate and washings, dilute to about 50 Cc., add 2 drops of methyl orange and titrate with the standard acid as in the case of the carbonates or hydroxides. One drop of the V.S. should change the transition tint to a distinct pink. Repeat the ignition and titration of another portion as a check. From the volume of standard acid consumed by the carbonate and its equivalent of the organic salt, calculate the percentage of the latter in the sample.

Illustration.—Potassium bitartrate, when carbonized, is changed into K_2CO_3.

$$\frac{2KHC_4H_4O_6}{2 \times 188.15} = \frac{K_2CO_3}{138.20} + xC + yH_2O + zCO_2.$$

Two (2) molecules of the bitartrate give one (1) of carbonate, or, $2 \times 188.15 = 138.20$. One molecule of carbonate requires 2 molecules of HCl for neutralization when methyl orange is used. The equivalent of K_2CO_3 is, therefore, 69.1 Gm. and corresponds to 188.15 Gm. of the bitartrate.

$$HCl = \frac{K_2CO_3}{2} = KHC_4H_4O_6. \quad \text{Therefore,}$$

1 Cc. of normal alkali $= 0.06910$ Gm. of $K_2CO_3 = 0.18815$ Gm. of $KHC_4H_4O_6$.

The calculation of the percentage is then made in the usual way. See p. 24. By representing the conversion of organic salts of the alkalies into carbonates in equations, the factor for any salt may be readily derived. The acetates, lactates, benzoates and salicylates behave like the bitartrates, two (2) molecules in each case producing one of the carbonate so that the equivalent of 1 Cc. will be in the case of normal acid V.S., $\frac{1}{1000}$ of the molecular weight, in grammes, of any one of these organic salts. For factors see p. 89.

The neutral tartrates, when decomposed by heat, form more carbonate than the salts of the monobasic acids or the bitartrate:

$$KNaC_4H_4O_6 = KNaCO_3 + xCO_2 + yH_2O + zC.$$

The equivalent of a neutral tartrate will, therefore, correspond to one half the molecular weight.

The neutral citrates are decomposed as represented:

$$2Na_3C_6H_5O_7 = 3Na_2CO_3 + xCO + yH_2O + zC.$$
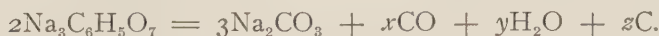
The equivalent of a neutral citrate corresponds to one third of the molecular weight of the particular salt determined.

Note: This method of titration may be extended to the determination of the organic salts of the alkaline-earths. The carbonates or oxides then produced being insoluble, residual titration has to be performed. See under insoluble carbonates and oxides.

6. DETERMINATION OF HYDROXIDES AND CARBONATES TOGETHER.

A. The Carbonate is Removed as $BaCO_3$. (Winkler's Method.)

1. Determine the total alkali present by titration of one portion of the solution of the sample with $\frac{N}{2}$ or $\frac{N}{10}$ HCl V.S.; indicator, methyl orange. The volume of the standard acid consumed (a) corresponds to hydroxide and carbonate.

2. To another, equal portion of the sample heated to boiling,[1] add an excess of a neutral, 10 per cent. $BaCl_2$ solution, heat for some time, let stand to deposit the $BaCO_3$ and then titrate with $\frac{N}{2}$ or $\frac{N}{10}$ acid, and phenolphthalein.

$$Na_2CO_3 + BaCl_2 = 2NaCl + BaCO_3.$$

The titration must be very carefully performed, and only few drops of the acid V.S. added at a time to prevent decomposition of the barium carbonate. The volume of the standard acid required (b) corresponds to the hydroxide. Subtracting (b) from (a) gives volume of standard acid corresponding to carbonate. The percentage of each ingredient is calculated from the volume of acid consumed by it in the usual manner just as in the determination of these compounds separately, care being taken to employ the proper factors.

Observations.—Instead of directly titrating in presence of the $BaCO_3$ formed, the mixture may be made up to measure a definite volume, aliquot portions filtered off through a dry filter paper and titrated. The water used for dilution should be free from CO_2. Since the volume of $BaCO_3$ is unknown, an error will be introduced in this operation. First portion of filtrate should be rejected.

The $BaCl_2$ in excess, reacting with the hydroxide present, produces an equivalent quantity of $Ba(OH)_2$, so that the alkalinity of the solution is not changed. A considerable excess of $BaCl_2$ should be added to decrease the hydrolysis of $BaCO_3$.

B. Titration with Two Indicators. (Warder's Method.)

Titrate a solution of a portion of the sample in the cold (near $0°$ C.) with the standard HCl, using phenolphthalein and stirring the mixture gently. The volume of the standard acid consumed (a) corresponds to hydroxide and one half of carbonate.

$$NaOH + HCl = NaCl + H_2O.$$

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \text{ (phenolphthalein)}.$$
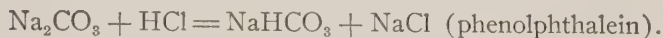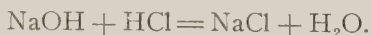
Then add to the titrated liquid 2 drops of methyl orange and titrate with the same standard acid to the production of reddish color. The volume of acid required in this titration (b) corresponds to one half of the carbonate.

$$NaHCO_3 + HCl = NaCl + CO_2 + H_2O \text{ (methyl orange)}.$$

[1] Soerensen and Andersen, Ztsch. Anal. Chem., 1908, 25, p. 279.

When (b) is subtracted from (a) the difference gives the volume of standard acid corresponding to hydroxide, while twice (b) corresponds to carbonate. From these volumes of the standard acid consumed the percentage of each compound to which they correspond is calculated by employing their proper factors.

Observations.—Method (B) is based on the behavior of the two indicators with carbonates and bicarbonates. Phenolphthalein reacts with CO_2, and, when the carbonate is converted into bicarbonate, the pink color of its ions disappears. Methyl orange, being practically not affected by CO_2, remains yellow until all carbonate or bicarbonate present is decomposed. However, an excess of CO_2 in solution is not entirely without effect on methyl orange so that for exact results, especially when weak standard V.S. are employed, the titrated liquid should be boiled when it becomes just pink, then cooled, more M.O. added and the titration completed.

Hydroxides and carbonates together may be also determined, though less accurately by titration with $\frac{N}{10}$ acid V.S. using as indicator phenacetolin. The V.S. is added to the solution of the sample until the yellow color produced by the hydroxide present is turned to red; the volume of the standard acid consumed corresponds to the hydroxide. The addition of the V.S. is then continued until the red color just changes to yellow; the volume of the second portion of standard acid V.S. corresponds to carbonate. The value for carbonate will be somewhat higher, and that for the hydroxide proportionally lower.

7. DETERMINATION OF CARBONATES AND BICARBONATES TOGETHER.

A. The Bicarbonate is Changed Into Carbonate by NaOH.
(Winkler's Method.)

1. Determine the total alkali in one portion of a solution of the sample by titration with $\frac{N}{2}$ or $\frac{N}{10}$ acid V.S., using methyl orange. The volume of standard acid consumed (a) corresponds to carbonate and bicarbonate.

2. To another equal portion of the solution add an excess of standard NaOH, V.S. preferably of the same strength as the acid V.S., using a volume exactly equal to that of acid consumed in (1), then add a neutral, 10 per cent. solution of $BaCl_2$ in excess and titrate carefully with the standard acid, using phenolphthalein. Subtract the volume of the standard acid V.S. used from the volume of standard NaOH V.S. added; the difference gives the volume of the NaOH V.S. (b) consumed by the bicarbonate.

$$NaHCO_3 + NaOH = Na_2CO_3 + H_2O.$$
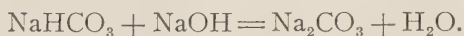
The volume of standard acid which corresponds to carbonate is found by subtracting (b) from (a). From these data the percentages of carbonate and bicarbonate are calculated by employing proper factors for these compounds.

Observations. — The reaction of hydroxide with bicarbonate, which shows why the two can not be present in the same solution,

is utilized in method A. To find how much bicarbonate a sample contains, a definite volume of standard NaOH V.S. is added, the carbonate then present removed by $BaCl_2$ and the unconsumed NaOH found by titration. The volume of the standard NaOH V.S. consumed, or an equal volume of a standard acid of the same strength, corresponds to the bicarbonate present. The NaOH V.S. should be of the same strength as the acid V.S.

B. Titration with Two Indicators.   (Warder's Method.)

Titrate a portion of sample in solution in the cold with $\frac{N}{2}$ or $\frac{N}{10}$ HCl V.S. in the presence of phenolphthalein, the tip of the burette being immersed in the titrated liquid. The volume of the standard acid V.S. consumed (a) corresponds to one half of the carbonate present.

$$Na_2CO_3 + HCl = NaHCO_3 + NaCl \text{ (phenolphthalein).}$$
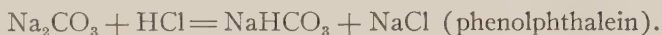
Then add to the titrated liquid methyl orange and titrate to the production of pink color. The volume of the standard acid required (b) corresponds to one half of the carbonate and all bicarbonate present.

$$NaHCO_3 + HCl = NaCl + H_2O + CO_2 \text{ (methyl orange).}$$

Subtract (a) from (b) to obtain the volume of standard acid V.S. corresponding to bicarbonate while twice (a) corresponds to the carbonate. From these calculate the percentage of each ingredient as usual.

Observations.—In method (B) the solution should be cold and the tip of the burette immersed, during titration, to prevent loss of CO_2.

This method may be employed for the determination, by titration, of aluminate and hydroxide of an alkali present together. Titrating with phenolphthalein, the standard acid V.S. corresponds to free alkali; with methyl orange to the alkali combined as aluminate.

Insoluble or Sparingly Soluble Bases.

8. Determination of Oxides and Carbonates.

Magnesium, calcium, barium, strontium, zinc, manganese, etc., oxides and carbonates.

Volumetric solutions employed: N or $\frac{N}{2}$ acid and N or $\frac{N}{2}$ alkali. Indicator: Methyl orange.

Weigh accurately 0.5 to 1.0 Gm. of the dry powdered sample into a titration flask or use the residue obtained by evaporation of a solution and ignition, or ignition of an organic salt, add to it an excess of the standard acid carefully measured (30 to 50 Cc.), mix well and let stand 10 minutes. If the sample is a carbonate, heat to remove the CO_2 in solution and cool. Add 2 drops of the indicator and titrate with the standard alkali V.S. In titration of

zinc compounds the alkali V.S. should be added in small portions and sufficient time allowed between additions for the precipitate $(Zn(OH)_2)$ to redissolve. When one drop of the alkali V.S. is found to produce a yellowish color which another drop added changes to yellow, the titration is ended. Confirm the results so obtained by another titration carried out in precisely the same manner and calculate the percentage of the particular compound present in the sample applying the rule on page 24.

Illustration.—To each of two portions of 1 Gm. of a sample of zinc oxide, 40 Cc. of N acid V.S. were added and the unconsumed acid required for its neutralization 32.3 Cc., and 31.8 Cc. of $\frac{N}{2}$ alkali V.S.; to calculate the percentage of ZnO in the sample.

The factor for ZnO with N acid is 0.04085 Gm., and is derived from the equation:

$$\underset{81.7}{ZnO} \;+\; \underset{2 \times 36.47}{2HCl} \;=\; ZnCl_2 \;+\; H_2O.$$

1 Lt. of N-HCl contains 36.47 Gm., and corresponds to 40.85 Gm. of ZnO. 1 Cc. of the V.S. is, therefore, the equivalent of 0.04085 Gm. of ZnO.

The factor (equivalent of 1 Cc. of N acid) is $= 0.04085$ Gm.

Volume of N acid added .... 40.0 Cc.
Volume of $\frac{N}{2}$ alkali required $= 32$ Cc., equal to N V.S... 16.0 Cc.
Volume of N acid consumed by 1 Gm. of sample........ 24.0 Cc.

$24 \times 0.04085 = 0.9804$ Gm. of ZnO in 1 Gm. of sample. By proportion,

$$1.0 : 0.9804 :: 100 : x.$$

$$x = \frac{0.9804 \times 100}{1.0} = 98.04.$$

The sample is found to contain 98.04 per cent. of zinc oxide.

Observations.—Bases, insoluble in water, do not affect indicators. To neutralize them completely requires an excess of the acid V.S. For these reasons the residual method of titration is employed in their determination. If, after standing and mixing for some time, the acid does not dissolve all of the sample taken for titration, more of the standard acid, carefully measured, should be added. Should this have no solvent action on the material the titration is carried on in the usual manner, as the presence of anything insoluble in the acid can not affect the results of the titration.

9. DETERMINATION OF ALKALINE-EARTH OXIDES AND CARBONATES.

1. The total amount of both ingredients is determined in one portion of the sample, by residual titration, as given on p. 64. The volume of the standard acid V.S. consumed by the sample (*a*) corresponds to oxide and carbonate.

6

2. In another equal portion of the sample the oxide is titrated with $\frac{N}{10}$ acid V.S. and phenolphthalein, the acid being added drop by drop to prevent decomposition of the carbonate. The volume of the standard acid required for this (*b*) corresponds to the oxide. When (*a*) is subtracted from (*b*) the volume of standard acid V.S., corresponding to carbonate, is obtained. The calculation of the percentage of each is then readily made.

10. DETERMINATION OF ALKALINE-EARTH BICARBONATES.
(Hehner's Method.)

One of the methods of determination of temporary hardness of water, which is due to the presence in it of bicarbonates of calcium and magnesium, is to titrate 100 Cc. of the sample with $\frac{N}{10}$ HCl, using methyl orange. The quantity of bicarbonate indicated is calculated into $CaCO_3$, and expressed in parts per 100,000. Permanent hardness due to the presence of other salts of the alkaline-earth metals, chiefly chlorides and sulphates, may be determined by evaporating 100 Cc. of the sample with an excess of $\frac{N}{10}$ sodium carbonate V.S., the volume being carefully measured, to dryness, extracting the residue with portions of distilled water, filtering and titrating the filtrate with $\frac{N}{10}$ acid V.S. The volume of standard Na_2CO_3 V.S. consumed by the salts in the sample is used for calculation of the permanent hardness.

$$MgCl_2 + Na_2CO_3 = MgCO_3 + 2NaCl.$$

Observations.—This titration for permanent hardness is of value only when no alkali carbonates are present in the water and, therefore, is not available for alkaline waters.

Hardness of water is usually determined by Clark's method in which a standard alcoholic solution of soap is employed. Soap is not decomposed by alkalies but, with alkaline-earth metals in solution, insoluble compounds are formed which do not produce lather on shaking. The soap solution should be freshly standardized with standard $CaCl_2$ solution. For total hardness the soap solution is added directly to a measured volume of the sample; for permanent hardness, to an equal volume of the sample after boiling, until, in each case, on shaking, a permanent lather is formed. From the larger volume of the standard soap solution consumed and from the difference of the two volumes which corresponds to the temporary hardness, the corresponding values for total and temporary hardness are obtained.

11. DETERMINATION OF SOLUBLE SALTS OF METALS PRECIPITATED BY SODIUM CARBONATE.

Volumetric solutions employed: $\frac{N}{10}$ sodium carbonate and $\frac{N}{10}$ HCl. Indicator: Methyl orange.

Dissolve a weighed quantity of the sample, placed in a measuring flask, in water, using a little dilute acid if necessary, and neutralize the liquid with NaOH solution, using methyl orange. Add an

excess of the $\frac{N}{10}$ sodium carbonate V.S., measuring its volume care-
fully, agitate the mixture until the precipitate becomes coarse and
settles readily. Dilute with water to the mark and filter off aliquot
portions for titration, using methyl orange. From the volume of
standard sodium carbonate V.S. consumed by the sample, calculate
the percentage of the salt sought, deriving the required factor
from an equation representing the involved reaction.

II. Organic Bases.

12. Determination of Alkaloids.

General Properties.—Alkaloids are the active constituents of cer-
tain vegetable drugs. They are basic in character and are present
in the plant parts combined with various acids as salts. Though
these alkaloidal salts are more or less soluble in water they can not
readily be separated from other ingredients in a state of purity,
while alkaloids (the bases) allow of practical isolation.

The activity or value of a potent drug which contains an alkaloid
or alkaloids is dependent directly on the amount of the alkaloid or
alkaloids it contains. Such drugs are therefore assayed or their
alkaloidal content is determined by analysis for purposes of valu-
ation.

The soluble inorganic bases including the carbonates and bicar-
bonates are much more strongly basic than the alkaloids, and when
added to their salts in aqueous solutions decompose them, liberating
the alkaloids. The solid alkaloids, when thus set free, separate as
a precipitate.

Solubility.—Most alkaloidal salts are soluble in water and the
presence of an acid is found to increase their solubility. The alka-
loids themselves do not dissolve in water, but will readily dissolve
in dilute acid, in which case, the alkaloid having formed a salt of the
acid, it is really the salt that is dissolved. The alkaloids dissolve
in certain other solvents known as "volatile solvents" such as:
alcohol, ether, chloroform, acetic ether, benzene, petroleum benzin,
etc., but not in carbon tetrachloride. Of these solvents those which
do not mix readily with water are called "the immiscible solvents."
Alkaloidal salts are, as a rule, insoluble in the immiscible solvents.
The separation and determination of alkaloids is based on these
differences of solubility of the alkaloids and their salts. The
immiscible solvents serve to separate and remove the alkaloids from
the solution of their salts, the alkaloids being set free by addition
of a soluble stronger base. Conversely, a solution of an alkaloid
in an immiscible solvent will, when shaken with dilute acid, yield
the alkaloid to the acid in which the alkaloidal salt formed readily
dissolves. The separation is, therefore, chemical as well as me-
chanical.

The " Shaking Out " Process.—To summarize, we see that solu-
tions of alkaloidal salts in water, or water slightly acidified, yield
their alkaloids to the immiscible solvents when such solutions are
made alkaline and thoroughly shaken with the solvent, and that the
alkaloid may be made to pass into the aqueous solution as a salt,

if the solution of it is strongly agitated with acidified water.   Intimate mixing is therefore essential for complete extraction, and is best brought about by shaking the two liquids in a closed vessel. When the two liquids have separated, the heavier may be drawn off or the lighter can be siphoned or poured off to separate them.

But, since the alkaloids are not entirely insoluble in water, especially when this is charged with the volatile solvent, while some of the alkaloidal salts are somewhat soluble in the volatile solvent saturated with water, the "shaking out" treatment is to be repeated several times with new portions of the solvent in order to make the separation complete.   Usually diminishing portions of the solvent are added and the shaking repeated until a small portion of the last extract gives no reaction when tested with a general alkaloidal reagent.

Testing for Alkaloids.—When an aqueous, or acid solution, is to be tested, few drops of the liquid are placed in a clean watch glass and a drop or two of mercuric potassium iodide solution (Mayer's Reagent) are added.   A white to yellowish precipitate forms with even a very small quantity of an alkaloid.
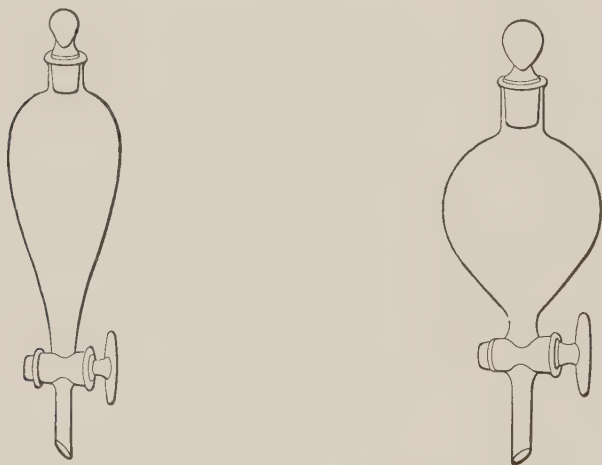
FIG. 27.   SEPARATORS.

Solutions of alkaloids in volatile solvents must be evaporated to dryness before testing.   Few drops of the liquid are allowed to evaporate spontaneously, or, if alcoholic, are evaporated on water-bath, residue taken up with 2–3 drops of N acid and when dissolved, the alkaloidal reagent is added.

Mercuric Potassium Iodide Solution.—Mercuric chloride, 1.344 Gm., dissolved in 60 Cc. of water is mixed with 5 Gm. KI dissolved in 10 Cc. of water and the solution diluted to measure 100 Cc.

Separation.—To facilitate the separation of the immiscible liquids, specially devised, glass vessels called "separators" are employed. Separators are conical or pear-shaped, Fig. 27, the neck provided with a well fitting glass stopper and the stem with a glass stopcock.

The stem should be short, and its end obliquely ground. When shaken, the contents of a separator often become warm due to the heat of the reaction, friction, or the heat of the hand. The pressure of the vapors within increases and should be occasionally relieved by holding the separator in an inverted position (stem up) and opening the stopcock temporarily. This is necessary to avoid loss of the contents which is apt to occur if the stopper should be blown out.

Concentration of the Solutions.—A solution of the alkaloidal salt to be treated for extraction by the " shaking out " process should not be very dilute. Though alkaloids, being weak bases, are ionizable to only a minute extent, their ionization becomes more appreciable the more dilute the solution. The volatile solvent in which the alkaloids do not ionize, dissolves out only nonionized molecules; for this reason the weaker the solution from which the alkaloid is to be shaken out, the larger the proportion of it will be retained in solution.

Again, the alkaloidal salts being those of weak bases are hydrolyzed to a greater or less extent, the free base though ionizing sparingly is held by the volatile solvent when shaken with an acid, and the larger the volume of solution used the more alkaloid is bound to remain in it. Acids or acid salts overcome this action to a marked degree; however, it has been lately observed that

Fig. 28. Percola-
tor arranged for
Filtration of Emul-
sions.

the alkaloidal salts, in the presence of acids are themselves more soluble in the immiscible solvents.

Emulsions.—Very vigorous shaking with an immiscible solvent is not always necessary to extract the alkaloids or their salts, and should be avoided in certain instances, especially when the sample is prone to form an emulsion. These emulsions always hold some of the alkaloid; most of them break up slowly if at all, within reasonable time and are otherwise troublesome to handle. Emulsions are less apt to form with chloroform, or a mixture of chloroform and ether than with ether alone. The tendency to emulsification may be minimized by shaking gently with a rotary motion of the separator or by increasing the difference in densities of the two liquids. When the solvent is largely chloroformic, more chloroform should be added; when ether is employed the aqueous liquid is made denser by the addition of pure sodium chloride to saturation. Cooling the separator and the contents has also been recommended. To break up an emulsion formed during shaking is not always an easy matter. Addition of NaCl to saturation or of its saturated solution is often effective; though evaporation on water-bath and stirring until the volatile solvent is removed is usually practiced. Addition of few drops of alcohol and filtration through cotton in a small percolator may be tried. The small percolator, Fig. 28, is prepared with absorbent cotton resting on a piece of platinum

wire (though glass wool will answer), the apparatus being arranged for suction filtration. If the emulsion should clog the percolator suction is applied. The cotton will retain the emulsifying agent (gum) and any alkaloid retained by it must be removed by washing with small portions of ether.

Rapid rotation in a centrifuge is an excellent means of separating many emulsions.

When a solution can not be shaken out without troublesome emulsification it may be extracted by perforation.

Purification of the Extracted Alkaloid.—Though it is possible to separate and remove, under proper conditions, from a drug or its preparations, practically all of the alkaloid contained therein, it is found that the first extract will contain, beside the alkaloid, many impurities such as resinous matters, extractives, fats, colors, etc., which are taken up by the solvent. In order to remove these impurities the alkaloid in solution in the immiscible solvent is converted into a salt by shaking with dilute acid, the salt formed being soluble in weak acid is taken up by it while most of the impurities remain in the volatile solvent. The acid solution of the salt, when made alkaline and shaken out with portions of the pure immiscible solvent, will give up the alkaloid to the latter, and this treatment if repeated will free the alkaloid effectively of all the impurities.

Alkaloidal Residues.—After the alkaloid of a drug has been completely separated, and if necessary purified, the analysis is completed by evaporation of the volatile solvent in which it is dissolved and weighing the alkaloidal residue or determining the alkaloid in the residue by titration. The alkaloidal residue is usually a varnish-like amorphous mass more or less impure from fats, resins, extractive matters, colors, soaps, etc. Unless its alkaloids are actually identified by proper tests, it is simply assumed to contain those alkaloids supposed to be contained in the drug assayed; this, it will be observed, need not be the case. The alkaloidal residue should be weighed only when it consists of the pure alkaloid or alkaloids which are being determined, though this is seldom the case. If the alkaloid is a liquid it should be converted into a salt (the hydrochloride) and weighed as such.

Weighing the alkaloidal residue would be preferable were it possible to purify it without material loss. Resort must therefore be had to the volumetric determination which, for certain drugs, is the only method available. It is, however, of advantage to weigh the residue even when it is to be titrated. When chloroform has been used as the solvent the alkaloidal residue is apt to hold ammonia which, if not removed would, in titration, consume some of the standard acid used. Ammonia is removed by dissolving the residue in 3 to 5 Cc. of pure ether and evaporating to dryness on a water-bath. Chloroform, if allowed to remain in contact with an alkaloid in solution during a longer period of time (over night), will decompose with the production of appreciable quantities of HCl and $COCl_2$. The HCl will neutralize some of the alkaloid, causing the volumetric results to be low while the gravimetric become high, the increase in weight being due to the salt formed.

However, the error due to this cause has been found very small and, according to H. Sumner (Arch. der Pharm., 1907, 627) may be regarded negligible.

Titration of Alkaloids.—The titration of alkaloids is residual, the volumetric solutions commonly employed are: $\frac{N}{10}$ acid, preferably sulphuric and $\frac{N}{50}$ alkali V.S. For most alkaloids the indicators employed are iodeosin[1] or cochineal, if the solution is colorless or nearly so, in which case hematoxylin or gallein may be also used. For lightly colored residues, or solutions, iodeosin is preferred to cochineal, the ethereal layer usually holding the coloring matters in solution. For very highly colored solutions, fluorescin is the best indicator.

Operation. (General Method.)—For titration, the alkaloid or alkaloids contained in the ethereal solution are obtained as a residue by evaporation of the ethereal extract to dryness. The residue which is usually resinous, is freed of ammonia if chloroform has been used, and is dissolved in a measured volume of $\frac{N}{10}$ (sometimes $\frac{N}{20}$) sulphuric acid, the acid being used in excess. For this from 3 to 5 to 15 Cc. of the standard acid will be found sufficient in ordinary cases, though this volume will depend on the quantity of sample and of alkaloid present. Should solution take place very slowly, gentle warming will be found to assist it materially, though in any case titration should be made only after at least 15 minutes were allowed for digestion. The proper indicator having been added, the unconsumed acid is titrated with the $\frac{N}{50}$ alkali V.S. At least two such titrations should be made for the purpose of checking results. It is important to perform these titrations with special attention to proper conditions, and all other details in which they should not differ. The end-reaction is seldom very sharp, due to the influence of the impurities present in the alkaloidal residue, and it is necessary to titrate to a distinct shade of color determined upon by a blank titration. The volume of the V.S. of alkali required to neutralize the excess of the standard acid is then converted into its equivalent of $\frac{N}{10}$, and this is then subtracted from the volume of acid added, the difference which represents $\frac{N}{10}$ acid consumed by a residue is used in calculating the percentage of the alkaloid. Calculation of the results differs in no way from those of other volumetric determinations, viz.:

$$\frac{\text{Cc. V.S. consumed} \times \text{Factor} \times 100}{\text{Weight sample}} = \text{percentage.}$$

The table of equivalents of alkaloids on page 90 gives these only for the tenth-normal acid. When a standard acid V.S. of other strength is used the proper factors may be readily derived from those given in the table.

Illustration.—Two 10 Gm. portions of belladonna leaves were extracted by maceration and percolation, the alkaloids shaken out and the residue left on evaporation of the volatile solvent, then titrated. In each case 4 Cc. of $\frac{N}{10}$ H_2SO_4 V.S. were added and the excess of

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[1] For titration in the presence of iodeosin, see under Indicators, p. 39.

acid titrated with $\frac{N}{50}$ alkali, using iodeosin. Of the standard alkali 14.7 Cc. and 14.3 Cc., respectively, were required; to calculate the percentage of alkaloids in the sample.

$$\text{Average of } \tfrac{N}{50} \text{ alkali V.S. required} = 14.5 \text{ Cc.}$$

$$\text{Converted into } \tfrac{N}{10} \text{ V.S.} = \frac{14.5}{5} = 2.9 \text{ Cc.}$$

$$\text{Tenth-normal acid added} = 4.0 \text{ Cc.}$$
$$\text{Tenth-normal acid unconsumed} = 2.9 \text{ Cc.}$$
$$\text{Tenth-normal acid consumed by alkaloids in residue} = 1.1 \text{ Cc.}$$

1 Cc. of $\frac{N}{10}$ acid V.S. $= 0.02892$ Gm. of belladonna alkaloids (see p. 90). $1.1 \times 0.02892 = 0.031812$ Gm. of alkaloids in the residue. Since 10 Gm. of sample were used, then by proportion:

$$10 : 0.031812 :: 100 : x.$$

$$x = \frac{0.031812 \times 100}{10} = 0.31812 \text{ per cent. of alkaloids in the sample.}$$

13. Assay of Drugs and their Preparations.

(a) Powdered Drugs.[1] (General Method of Treatment.)—A suitable quantity, 5 to 20 Gm., of the drug in fine (No. 60) or very fine (No. 80) powder is macerated in a flask, bottle or mixing cylinder provided with a well-fitting stopper. The immiscible solvent employed is ether, chloroform or a mixture of these sometimes with a small portion of alcohol. (Prollius fluid.) As a precipitant for the alkaloid ammonium hydroxide, 10 per cent., is the most commonly used alkali except in an assay of physostigma when sodium bicarbonate solution is employed. The precipitant is either added to the solvent before maceration or is introduced after the solvent and drug have been mixed. The quantity of the solvent needed differs with the character of the drug itself as well as with the quantity of sample taken and the method followed. It is important to use the right quantity of the solvent; especially, in those assays in which an aliquot portion of the ethereal solution is to be used for subsequent treatment, is the volume of the solvent to be accurately measured. Maceration, with occasional shaking, requires from 1 to 12 hours; the time may, however, be shortened to 4 hours by the use of a mechanical shaker. To clarify the resulting turbid mixture, a small quantity of water which causes the powder to collect in masses, is sometimes added.

The function of ammonium hydroxide is to liberate the alkaloids in the presence of the solvent which is ready to take them up and hold them in solution; so that in this process the alkaloids are supposed to be completely extracted. Two methods of subsequent treatment are now open.

[1] Opium and its preparations require a different method of treatment, morphine being almost insoluble in the immiscible solvents.

(1) The mixture is transferred to a small percolator and the drug completely exhausted by percolation with more of the menstruum, and the ethereal solution subjected to the shaking-out treatment (assay of belladonna, hyoscyamus, stramonium, scopola, cocoa).

(2) A portion of the ethereal solution corresponding to a given weight of the drug is drawn off, if clear, by means of a pipette or, if turbid, is filtered off, and the ethereal solution subjected to the shaking-out process. (Assay of cinchona, colchicum, conium, hydrastis, nux vomica, pilocarpus.)

Weighing of the aliquots has been recommended. It will be evident that if this is to be practiced the solvent taken for maceration must also be weighed. Of these two procedures the complete extraction by percolation is the more reliable. By taking an aliquot, whether by measuring or weighing the ethereal solution, an error is introduced. If, for example, 15 Gm. of a drug were macerated with 150 Cc. of the menstruum and 100 Cc. of the ethereal solution were drawn off, it is evident that these 100 Cc. correspond to 10 Gm. of the drug and the supposition is that they also contain all the alkaloids from 10 Gm. of the sample. This is hardly ever true. With no loss of the solvent during maceration and measuring, the amount of alkaloids in 100 Cc. of the ethereal solution will be less than is present in 10 Gm. of the drug, on account of the dissolved impurities and the absorption of water. When, however, some of the solvent has been lost by evaporation and this is often unavoidable, then through concentration of the solution the proportion of alkaloids in it will become increased and will be more than the 10 Gm. contained.

The ethereal solution is usually shaken out with N or diluted sulphuric acid (hydrochloric, hydrobromic and nitric acid salts of alkaloids are more soluble in volatile solvents than those of sulphuric, phosphoric, tartaric or citric acids) or the solution is evaporated to dryness, and the alkaloids in residue taken up with N sulphuric acid and water. From the acid solution the alkaloid is shaken out with chloroform or ether after the solution has been made alkaline. The assay is then completed by weighing the residue obtained by evaporation of the solution on water-bath or the residue is dissolved in 3–15 Cc. of $\frac{N}{10}$ H_2SO_4 V.S. and the excess of acid titrated with $\frac{N}{50}$ alkali V.S.

(b) **Extracts, Resinoids, etc.**—Powdered extracts are mostly treated like the powdered drugs, the quantity used for assay being diminished in proportion to their strength. Solid or soft extracts are preferably dissolved in appropriate menstruum, then freed of alcohol by partial evaporation or evaporated to dryness with clean sand and the residue treated with the volatile solvent as are the drugs.

(c) **Fluidextracts.**—Certain fluidextracts are treated directly in a separator with the volatile solvent and the base which liberates the alkaloids, or, after dilution with water, are shaken out with the immiscible solvent. In other cases the alcohol is removed by evaporation to dryness at low temperature (aconite, ipecac, nux vomica) or evaporated with clean sand (conium, pilocarpus), the

residue taken up with dilute acid and subjected to the shaking-out process.

(d) **Tinctures.**—Some tinctures are dealcoholized and concentrated by evaporation to $\frac{1}{10}$ volume and then shaken out with dilute acid (belladonna, cinchona, colchicum seed, hydrastis, hyoscyamus, stramonium). The evaporation may be carried on to dryness and the residue taken up with dilute acid (aconite, nux vomica, physostigma). Other tinctures are treated like the corresponding fluidextracts or extracts.

(e) **Syrups.**—For the extraction of alkaloids from syrups, Dragendorff's Reagent[1] has been used. Of the sample 20 Cc. or, if percentage is required, 20 Gm. are mixed with 50 Cc. of water, 15 Cc. of 10 per cent. sulphuric acid, 5 Cc. of the reagent added, mixed, and left to remain over night (12 hours). The precipitate is collected on a quantitative filter paper, previously moistened with dilute H_2SO_4, and washed twice with 10 per cent. sulphuric acid, allowing to drain each time. The filter paper and contents are then transferred to a 100 Cc. mixing cylinder, about 0.3 Gm. of sodium sulphite and 30 Cc. of 15 per cent. NaOH solution added and the mixture well shaken. Now about 15 Gm. of NaCl and exactly 50 Cc. of anhydrous ether are introduced and the securely stoppered cylinder shaken, at intervals, during 12 hours. When the two liquids have finally separated, 25 Cc. of the clear ethereal solution are drawn off (corresponding to 10 Cc. or 10 Gm. of sample), the ether allowed to evaporate and the residue titrated, using 5 drops of cochineal tincture.

(f) **Glycerites.**—From a solution in glycerin the alkaloids may be separated by precipitation with Wagner's reagent $(I + KI$ solution) the precipitate filtered off, decomposed with SO_2 and the free alkaloids shaken out with the immiscible solvent, the assay being completed as directed under the respective drug.

(g) **Ointments.**—Ointments are dissolved in the immiscible solvent and the solution is repeatedly shaken out with dilute sulphuric acid. Any residue, insoluble in ether, is taken up with dilute sulphuric acid, the acid solution made alkaline, extracted with ether or chloroform or a mixture of these, and the solution then mixed with the ethereal solution of the larger portion.

14. THE LLOYD'S METHOD OF ASSAY.

The separation of alkaloids from fluidextracts, solutions of extracts, or concentrated tinctures, is carried out with chloroform in presence of ferric hydroxide, the liberating agent being a bicarbonate. The ferric hydroxide serves to retain coloring and extractive matters, acids, tannin, etc. The ferric hydroxide is formed, *in situ,* by sodium bicarbonate which also liberates the alkaloids. Of a sample of fluidextract usually 5 Cc., accurately measured, are mixed with 2 Cc. of a solution of ferric chloride (U.S.P. strength) in a small mortar and the $NaHCO_3$ then added in powder until, on mixing, a firm paste results. The alkaloids are extracted by

[1] For composition see 16, page 75.

repeated trituration with portions of chloroform, until the final extractions are found free from alkaloids. The chloroformic solution is then shaken out with dilute acid and this, when made alkaline, again with chloroform or it may be evaporated to dryness and the alkaloidal residue treated as in other assays.

The chloroformic solution of the alkaloids is, as a rule, remarkably free from color and most other impurities, yet the method has several drawbacks which overbalance this advantage. The extraction consumes much time and considerable loss of chloroform results, while complete exhaustion of the sample is by no means assured. It has been pointed out also, that sodium bicarbonate does not precipitate strychnine, brucine or veratrine.

As decolorizing agent, lead subacetate is used for highly colored liquids and has been lately employed for the assay of opium and hyoscyamus. When used, a solution of it is added in excess and the lead in the filtrate is removed by H_2S or Na_2SO_4, or with $\frac{N}{10}$ oxalic acid as in the assay of opium, or by Na_2HPO_4 as with hyoscyamus.

15. Gordin's Method of Titration of Alkaloids.

Volumetric solutions employed: $\frac{N}{20}$ acid and $\frac{N}{20}$ alkali.

Indicator: Phenolphthalein.

To the alkaloidal residue to be titrated, an excess of $\frac{N}{20}$ HCl is added, the volume accurately measured, then an alkaloidal precipitant (Mayer's or Wagner's reagent) is added in slight excess and the mixture made to measure exactly 100 Cc. After settling, 50 Cc. of the clear liquid, corresponding to one half of the residue, are filtered off and, if Wagner's solution has been used, decolorized with 10 per cent. sodium thiosulphate, and the acid in excess titrated with $\frac{N}{20}$ alkali V.S. using phenolphthalein. From the volume of $\frac{N}{20}$ HCl consumed by the alkaloid, the percentage of it in the sample is calculated. The alkali V.S. must of necessity be free from carbonate.

16. Alkaloids by Potassium-Bismuth Iodide.

(Dragendorff's Reagent.)   Method of Thoms.

Volumetric solution employed: $\frac{N}{100}$ hydrochloric acid.

Indicator: Iodeosin.

The reagent: Dissolve 80 Gm. of bismuth nitrate in 200 Cc. nitric acid sp. gr. = 1.18, and pour this solution into a concentrated solution of 272 Gm. of potassium iodide in water. Let stand to separate KNO_3 and dilute the clear solution to measure 1000 Cc.

The alkaloid to be determined should be in the form of sulphate. A suitable quantity of the alkaloidal salt, or the alkaloidal residue obtained by extraction with a volatile solvent and evaporation, is dissolved in a little diluted sulphuric acid, an excess of the reagent added (about 10 Cc.), the contents of the vessel well mixed and filtered. The precipitate is washed with 10 Cc. of 5 per cent. sulphuric acid, transferred with the filter paper to a 100-Cc. mixing

cylinder, 10 Cc. of 10 per cent. NaOH, 10 Gm. of crystalline sodium carbonate added and the mixture shaken during 10 to 15 minutes. Then 50 Cc. of anhydrous ether, accurately measured, are introduced and the shaking continued for 20 minutes. By means of a pipette, 25 Cc. of the clear ethereal solution are carefully transferred to 250-Cc. flask, provided with a well fitting stopper, in which 100 Cc. of distilled water were previously mixed with 5 drops of iodeosin and 20 Cc. of ether and the red color of the water just discharged with a few drops of $\frac{N}{100}$ HCl V.S. The flask is then closed, the contents well mixed by shaking, and the alkaloid titrated with the $\frac{N}{100}$ HCl V.S. From the volume of the standard acid consumed the percentage of the alkaloid present is calculated.

To assay extracts by this method, 4 Gm. of the sample are shaken with 50 Cc. of 90 per cent. alcohol during three hours and the mixture filtered. One half (25 Cc.) of the filtrate is evaporated sufficiently to remove all alcohol, 10 Cc. of 10 per cent. sulphuric acid added followed by 5 to 10 Cc. of the reagent and the assay proceeded with as given above except that 20 Cc. of 15 per cent. NaOH are used, the Na_2CO_3 omitted, and the shaking with ether continued during three hours.

17. DETERMINATION OF PYRIDINE.

Ordinary indicators not reacting with pyridine, the methods of titration must be modified accordingly. One such modification utilizes the reaction of pyridine with ferric salts in which ferric hydroxide is formed:

$$FeCl_3 + 3C_5H_5N + 3HOH = Fe(OH)_3 + 3C_5H_5N \cdot HCl.$$
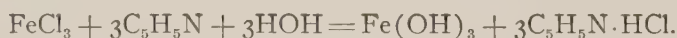
A weighed quantity of the sample of pyridine, diluted with water, is added to a neutral solution of ferric chloride in excess and the mixture well agitated. The ferric hydroxide formed is then titrated with N acid V.S., which is added slowly and carefully until the ferric hydroxide is just dissolved. From the volume of the standard acid consumed the quantity of the base is calculated in usual manner.

1 Cc. of N acid corresponds to 0.07906 Gm. of pyridine.

If, however, patent-blue be used as indicator, pyridine may be titrated directly in ethereal solution as recommended by Millbauer and Stanek. (Ztsch. anal. Chem., 1904, 43, 217.) The indicator with bases gives = blue; with acid = yellow-green. See Pyridine in Ammonia.

18. PYRIDINE IN AMMONIUM HYDROXIDE.

(Indicator, Patent-Blue V, N.)

Of the sample 100 to 200 Cc. are diluted with an equal volume of water, a drop of the indicator is added and then diluted with sulphuric acid until neutralized. The solution is then cooled, 10 to 15 drops of Na_2CO_3 solution added, and the liquid shaken with ether in three successive portions. The total ethereal solution is filtered and shaken with a measured volume of $\frac{N}{10}$ sulphuric acid V.S. used

in excess, the indicator added and the excess of the acid determined by titration with $\frac{N}{10}$ NaOH in the presence of pure sodium chloride which is added to saturation of the aqueous portion of the liquid. From the volume of standard acid consumed by the pyridine, the percentage of it in the sample is calculated.

1 Cc. of $\frac{N}{10}$ acid corresponds to 0.007906 Gm. of pyridine.

Ammonium salts are dissolved and treated as ammonium hydroxide. When the quantity of pyridine present is very small, the acidified solution of the sample is evaporated to dryness on water-bath and the residue extracted with alcohol. After the alcoholic solution has been acidified and the alcohol removed by distillation, the alcoholic residue is then taken up with water and treated as above.

B. ACIDIMETRY.

The determination of acids and acid-salts, by means of standard V.S. of the alkalies, is known as acidimetry. Most of the organic acids, but only the stronger inorganic, are determined by titration; the other inorganic acids are more accurately determined by other methods which will be noted in due order.

I. The Inorganic Acids.

19. DETERMINATION OF THE STRONGER ACIDS.

Hydrochloric, nitric, sulphuric, phosphoric, hypophosphorous; also hydrobromic, hydriodic and hydrofluoric, though these are best determined by precipitation. See Chapter III.

Volumetric solutions employed: N, $\frac{N}{2}$ or $\frac{N}{10}$ alkali.

Indicator: Methyl orange.

Weigh accurately (see note) a suitable quantity of the sample (3 to 5 Gm. of concentrated 10 to 15 Gm. of the dilute acid) dilute it with water to a definite volume at standard temperature and titrate aliquots with the standard alkali V.S. Dilute each portion to measure 50 Cc., add 2 drops of the indicator and run in the V.S. in small portions at first, reducing the flow to drops towards the end of the reaction. When the red color of the titrated liquid takes on an orange or almost yellow tint, discontinue the addition of the V.S., read the burette and accept the reading only if another drop of the V.S. is found to produce a pure yellow color. Should more than one drop of the alkali V.S. be required to produce the end-reaction, the alkali V.S. should be added in this cautious manner and the reading taken just before the final drop is added. From the average of at least two closely agreeing titrations the percentage of the particular acid in the sample is calculated.

Illustration.—Of a sample of nitric acid, 2.5 Gm. portions required an average of 36.5 Cc. of $\frac{N}{2}$ NaOH V.S.; to calculate percentage of absolute HNO_3 in the sample.

The factor of HNO_3 (equivalent of 1 Cc. of $\frac{N}{2}$ alkali V.S.) is 0.03151 Gm., and is derived from the equation:

$$\underset{63.02}{HNO_3} + \underset{40.01}{NaOH} = NaNO_3 + H_2O.$$

40.01 parts of NaOH react with, or neutralize, 63.02 parts of HNO_3. Since 1 Lt. of $\frac{N}{2}$ NaOH V.S. contains 20.015 Gm. and corresponds to 31.51 Gm. HNO_3,

1 Cc. of the V.S. is the equivalent of 0.03151 Gm. HNO_3.

The factor being = 0.03151 Gm. and since 36.5 Cc. of $\frac{N}{2}$ alkali were used, $36.5 \times 0.03151 = 1.150115$ Gm.

$$2.5 : 1.150115 :: 100 : x.$$

$$x = \frac{1.150115 \times 100}{2.5} = 46.00 + \text{per cent.}$$

The sample of nitric acid is found to contain 46.00 per cent. of HNO_3.

Notes.—Dilution of strong sulphuric acid should be performed with proper care and the acid poured into water.

The acid taken for analysis need not be weighed if its exact specific gravity is known. Since the determination of exact Sp. Gr. necessitates accurate weighing, little is gained by such procedure. Specific gravity taken with an areometer is, however, a useful indication of the quantity of the sample to be taken for titration.

Titration of acids is interfered with by ferric salts when these are present. To overcome their undesirable influence, C. C. Ahlum (Tr. Chem. Soc., 1906, V. 89) recommends the addition of sodium dihydrogen phosphate (NaH_2PO_4) solution of standard strength. The precipitate of $FePO_4$ is filtered off, and the acidity of the filtrate found by titration. From the quantity of Fe present (separately determined), the amount of acid due to its reaction with the phosphate is calculated and when this is deducted from the total acid found by titration of the filtrate, the quantity of acid present in the sample is obtained. In titration, methyl orange is used as indicator.

20. DETERMINATION OF BORIC ACID.

Volumetric solution employed: $\frac{N}{2}$ NaOH free from CO_2.
Indicator: Phenolphthalein.

Accurately weigh about 2 Gm. of the sample, dissolve it in 50 Cc. of water, add 50 Cc. of neutral glycerin, then 2 drops of the indicator, and titrate with the standard alkali V.S. to the production of pink color. From the volume of the NaOH V.S. consumed calculate the percentage of boric acid in the sample. The factor for boric acid with $\frac{N}{2}$ alkali V.S. is 0.031015 Gm., and is derived from the following equation:

$$\underset{62.03}{H_3BO_3} + \underset{40.06}{NaOH} = NaBO_2 + 2H_2O.$$

1 Lt. of $\frac{N}{2}$ NaOH V.S. contains 20.03 Gm. and corresponds to 31.015 Gm. H_3BO_3.

1 Cc. of the V.S. is the equivalent of 0.031015 Gm. H_3BO_3.

21. Determination of Borax Through Boric Acid.

Volumetric solutions employed: $\frac{N}{2}$ acid and $\frac{N}{2}$ NaOH **free from** CO_2.

Indicators: Phenolphthalein and methyl orange.

Dissolve 1 Gm. of the sample (uneffloresced salt) in 30 Cc. of water, in a medium flask, add 2 drops of M.O. and run in the $\frac{N}{2}$ acid until a rose-red color is produced. Boil the liquid under a return condenser, Fig. 29, 5 minutes, cool, rinse the condenser with small portions of recently boiled distilled water and neutralize any free acid by careful addition of the $\frac{N}{2}$ alkali V.S. To the titrated liquid, which has been made yellow by one drop of the V.S., add 50 Cc. of neutral glycerin, two or three drops of phenolphthalein and titrate with the $\frac{N}{2}$ alkali to distinct pink color. From the volume of the standard alkali required to neutralize the boric acid in the liquid, calculate the percentage of borax in the sample. To calculate borax from the boric acid titrated, the ratio of their molecules is first established from the equation:

$$\frac{4H_3BO_3}{4 \times 62.03} = \frac{Na_2B_4O_7 \cdot 10H_2O.}{382.20}$$
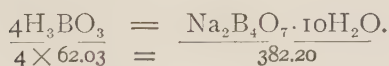
1 Lt. of $\frac{N}{2}$ alkali corresponds to 31.015 Gm. of H_3BO_3, and also to 47.7650 Gm. borax.

1 Cc. of $\frac{N}{2}$ alkali is, therefore, the equivalent of 0.0477650 Gm. of $Na_2B_4O_7 \cdot 10H_2O$.

Observations.—Boric acid is neutral to methyl orange and can not be titrated when this indicator is used. With phenolphthalein, the end-reaction, which takes place when one of the three hydrogens of the molecule is replaced by a metal, is uncertain on account of the hydrolytic action of water on the product of the reaction. To overcome

Fig. 29.   Heating under Return Condenser.

this action, glycerin is added (mannite is claimed to be even better), the end-reaction being in its presence sharp and correct. The quantity of glycerin needed is proportional to the volume of the titrated liquid and may be regulated by adding the glycerin in portions until it ceases to discharge the red color of the alkali-phenolphthalein at the end of the titration. The reason for the required absence of CO_2, from the V.S. as well as from the

titrated liquid, is obvious. When the sample itself contains CO_2, this gas must be removed by boiling under return condenser to prevent loss of boric acid, which is volatile with water vapor.

Borates are alkaline to methyl orange. When an acid is added to a solution of a borate in presence of methyl orange, the red color of the end-reaction appears only when the boric acid of the borate has been liberated. The acid acts on phenolphthalein and is titrated in the presence of that indicator. In the absence of other bases or interfering compounds, borates may be determined alkalimetrically.

Boric acids and borates, present *in foods* as preservatives, may be determined by titration in the manner just given for borax, after the sample has been properly prepared. To prepare the sample, 100 Gm. of the material are made distinctly alkaline with NaOH, evaporated to dryness in a platinum dish and the dry residue ignited. The ash is heated with 20 Cc. of water, few drops of HCl are added to dissolve it and, to the solution, transferred to a 100-Cc. flask, is added 0.5 Gm. of $CaCl_2$. After neutralizing the solution with $\frac{N}{5}$ NaOH, 25 Cc. of lime water are added and the mixture made up to 100 Cc. After the mixture has been well shaken, 50 Cc. are filtered off through dry filter paper and titrated with N sulphuric acid V.S., using methyl orange. When a distinct pink color has been produced, the solution is subjected to boiling under return condenser, etc., the method for borax being followed from this point on.

In butter, boric acid is determined by extraction with hot water and titration. For extraction, a rather large quantity of the sample (25–30 Gm.) is heated with water in a wide-mouth flask, provided with a stopper, and the usual wash bottle tubes. When the butter has melted the contents are agitated, allowed to separate and the aqueous layer is removed to a dish by blowing air into the flask. The extraction is repeated several times or until the extract gives no reaction with turmeric paper. The aqueous extract is then made alkaline, evaporated to dryness, the residue ignited and treated as described for the residue obtained from the other food stuffs.

22. Determination of Phosphoric Acid.

Volumetric solution employed: N alkali or $\frac{N}{2}$ NaOH, free from CO_2.

Indicators: Methyl orange or phenolphthalein.

Titrate a suitable quantity of the sample, diluted with water to measure 20 Cc., with the standard alkali V.S. and methyl orange, adding sufficient of pure NaCl to saturate the titrated liquid. With methyl orange the acid is monobasic and the reaction is completed when one third of its hydrogen is replaced by a base as represented in the equation:

$$\underset{98.03}{H_3PO_4} \;+\; \underset{40.01}{NaOH} \;=\; NaH_2PO_4 \;+\; H_2O.$$

With M.O. 40.01 Gm. of NaOH correspond to 98.03 Gm. of H_3PO_4, so that the factor for N-V.S. is based on:

$$\frac{98.03}{1000} \text{ corresponds to } \frac{40.01}{1000} = 0.09803 \quad \text{Gm. Phosphoric acid.}$$

$$\text{1 Cc. N alkali} = 0.09803 \quad \text{Gm. Phosphoric acid.}$$
$$\text{1 Cc. } \tfrac{N}{2} \text{ alkali} = 0.049015 \quad \text{Gm. Phosphoric acid.}$$

Titrate in like manner, another portion of the sample with $\tfrac{N}{2}$ NaOH, free from CO_2, adding NaCl and phenolphthalein. The end-reaction takes place when two thirds of the hydrogen of the acid are replaced by a base, according to the following representation:

$$\underset{98.03}{H_3PO_4} + \underset{2 \times 40.01}{2NaOH} = Na_2HPO_4 + 2H_2O.$$

With phenolphthalein 40.06 Gm. of NaOH correspond to 49.015 Gm. of H_3PO_4. The factor for N-V.S. is

$$\frac{49.015}{1000} = 0.049015 \quad \text{Gm. of Phosphoric acid.}$$

$$\text{1 Cc. N alkali} = 0.049015 \quad \text{Gm. of Phosphoric acid.}$$
$$\text{1 Cc. } \tfrac{N}{2} \text{ alkali} = 0.0245075 \quad \text{Gm. of Phosphoric acid.}$$

The same portion of the sample may be titrated with both indicators if, after the red of M.O. is just changed to yellow by the volumetric alkali, phenolphthalein is added and the titration continued until bright red color is produced. The volume of the alkali V.S. used with each indicator corresponds to one third of the acid present, the sum of these volumes corresponding to two thirds of it. The factors used for separate titrations of phosphoric acid, with the two indicators, are also used in this case, the total volume of the standard alkali consumed being regarded as being used with phenolphthalein. On account of the action of CO_2 on phenolphthalein the $\tfrac{N}{2}$ NaOH, free from CO_2 V.S., should be used when both indicators are employed and any CO_2, in the titrated liquid, removed by boiling.

Observations.—Sodium chloride is added to decrease ionization of the acid salts produced in the reaction. In place of it neutral $CaCl_2$ solution has been recommended. The acid salts formed in the reaction of phosphoric acid and an alkali, hydrolyze, forming ions which make the end-reaction indefinite, and results uncertain. Good results are said to be obtained by titration in the presence of iodeosin with which the acid is monobasic. If the acid be titrated, in the presence of M.O. or p-nitrophenol, with $\tfrac{N}{10}$ or $\tfrac{N}{50}$ $Ba(OH)_2$ V.S., a sharp end-reaction is obtained. For this titration the sample should be diluted to about $\tfrac{N}{5}$ strength.

By residual titration, phosphoric acid may be determined by titrating the precipitate of NH_4MgPO_4, or the filtrate from it. If the

7

filtrate is to be titrated, magnesia mixture[1] of recently determined alkalinity (by titration with standard acid) is added and the precipitation carried out in a closed flask or bottle. After thorough shaking the mixture is filtered and aliquots of the filtrate titrated with $\frac{N}{10}$ H_2SO_4 V.S. and methyl orange.

The NH_4MgPO_4, washed free from NH_4OH, may be treated with an excess of $\frac{N}{10}$ sulphuric acid V.S. and the acid in excess titrated with standard alkali V.S.

23. DETERMINATION OF H_3PO_4 AND THE SOLUBLE PHOSPHATES. (Method of Raschig.)

Volumetric solution employed: $\frac{N}{10}$ HCl or H_2SO_4.
Indicator: Methyl orange.
A suitable quantity of the sample, containing not more than 0.15 Gm. of P_2O_5 is carefully weighed, dissolved in a very small volume of water, the solution made weakly alkaline with NH_4OH and magiesia mixture[1] added in excess. After shaking well during one half hour, the precipitate is filtered off through a 4-Cm. filter paper, the filtrate being used to bring the rest of the precipitate on the filter paper, and the precipitate drained by suction. The precipitate is washed first with 10 Cc., then with 5 Cc. of cold water, transferred with the filter paper to a beaker, 20 Cc. of water added, two drops of methyl orange introduced and the mixture titrated with $\frac{N}{10}$ acid V.S. while it is being well mixed. One drop of the V.S., finally added, should produce a distinct pink color. From the acid consumed the percentage of phosphoric acid in the sample is calculated. The reaction involved is represented:

$$ \underset{137.37}{NH_4MgPO_4} + \underset{2 \times 36.47}{2HCl} = MgCl_2 + NH_4H_2PO_4. $$
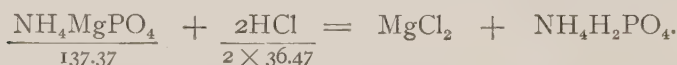
1 Lt. of $\frac{N}{10}$ HCl contains 3.647 Gm., and corresponds to 6.8685 Gm. NH_4MgPO_4.

1 Cc. of the V.S. is the equivalent of 0.0068685 Gm. NH_4MgPO_4.
The factor with $\frac{N}{1}$ acid is for $P_2O_5 = 0.00355$ Gm. of P_2O_5.
Phosphoric acid may also be determined by iodometric titration (method of Christensen). The acid liberates from KI with $KBrO_3$ an equivalent quantity of iodine which is titrated with standard thiosulphate V.S. See iodometric methods, Chapter III.
Phosphoric acid and phosphates are determined by titration with standard uranium acetate V.S. See Chapter IV.

24. DETERMINATION OF HYDROFLUORIC ACID.

Volumetric solutions: $\frac{N}{2}$ alkali free from CO_2 and $\frac{N}{2}$ H_2SO_4.
Indicator: Phenolphthalein.
Measure out the acid into a platinum dish by means of a pipette coated with wax (the capacity of the pipette is afterward ascertained), add an excess of the standard alkali, heat to boiling, drop

[1] Magnesia mixture contains $MgCl_{25}$, NH_4Cl_{10} and NH_4OH 10 per cent.

in the indicator and titrate the excess of the alkali with the standard acid V.S.

$$\underset{20.01}{HF} + \underset{40.01}{NaOH} = NaF + H_2O.$$

1 Cc. of $\frac{N}{2}$ NaOH V.S. is the equivalent of 0.010005 Gm. of HF.

25. Determination of Hydrofluosilicic Acid.

Volumetric solutions: N-KOH or Ba(OH)$_2$.
Indicator: Phenolphthalein or lacmoid.
Mix a suitable quantity of the sample with an equal volume of alcohol and, having added the indicator, titrate in usual manner.

$$\underset{144.32}{H_2SiF_6} + \underset{2 \times 56.11}{2KOH} = K_2SiF_6 + 2H_2O.$$
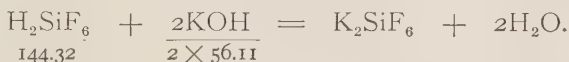
1 Cc. of N KOH corresponds to 0.07216 Gm. of H$_2$SiF$_6$.

Observation.—Sodium hydroxide, forming a hydrolizable salt with hydrofluosilicic acid, can not be used for its titration. If, however, an excess of CaCl$_2$ be used, standard NaOH and methyl orange may be employed, the reaction in that case is:

$$H_2SiF_6 + 3CaCl_2 + 6NaOH = 3CaF_2 + 6NaCl + H_4SiO_4 + 2H_2O.$$

26. Determination of Ammoniated Mercury. (NH$_2$HgCl.)

Volumetric solution: $\frac{N}{10}$ HCl.
Indicator: Methyl orange.
Weigh from 0.2 to 0.3 Gm. of the sample accurately, triturate with a small portion of water, repeat the trituration and transfer the fine particles in suspension to a glass-stoppered bottle, washing the mortar with water and using in all about 50 Cc.. Add to the mixture in the bottle 2 to 3 Gm. of KI and shake contents well during 10 minutes or until a clear solution results. To this add 2 drops of the indicator and titrate with the $\frac{N}{10}$ HCl so that finally one drop of the V.S. is found to produce a pink color. Having checked the results of this by another titration, calculate the percentage of ammoniated mercury from the volume of the standard acid consumed. The equivalent of 1 Cc. of $\frac{N}{10}$ HCl is 0.012574 Gm. and is obtained from the equations:

$$\underset{2 \times 251.49}{2NH_2HgCl} + 4KI + 4H_2O = HgI_2 + 2KCl + 2KOH + 2NH_4OH.$$

$$2KOH + 2NH_4OH + \underset{4 \times 36.47}{4HCl} = 2KCl + 2NH_4Cl + 2H_2O.$$
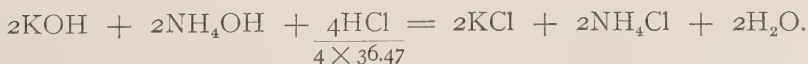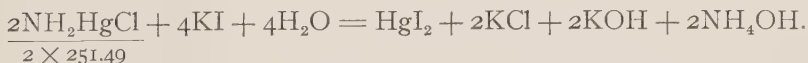
4×36.47 parts of HCl are consumed by the alkalies formed in reaction of 2×251.49 parts of ammoniated mercury.

1 Lt. of $\frac{N}{10}$ HCl contains 3.647 Gm., and corresponds to 12.5745 of NH$_2$HgCl.

1 Lt. of the V.S. is the equivalent of 0.0125745 Gm. of NH_2HgCl.

1 Cc. of $\frac{N}{10}$ acid $= 0.0125745$ Gm. of ammoniated mercury, or expressed as mercury, 1 Cc. of $\frac{N}{10}$ acid $= 0.01$ Gm. of mercury.

II. Organic Acids.

27. DETERMINATION OF THE STRONGER ORGANIC ACIDS.

Acetic, oxalic, lactic, citric, tartaric, trichloracetic acids, and the acid salts of those forming them.

Volumetric solutions employed: $\frac{N}{2}$ alkali, free from CO_2, or $\frac{N}{10}$ $Ba(OH)_2$.

Indicator: Phenolphthalein.

Accurately weigh, for each titration, about 1 Gm. of the sample (if diluted solution, proportionally more), dissolve, dilute to measure 50 Cc., and heat to boiling except in the case of acetic acid, for which see note below. Add to the solution 2 to 3 drops of the indicator and titrate with the standard V.S. which should be run in slowly in small portions. When the red color produced by the standard alkali begins to disappear only on mixing, reduce the flow to drops and add these carefully so that one drop of the V.S. is found to produce a reddish color, which another drop should intensify to a distinct and permanent pink. To check the result, carry out another titration in this manner and from the average of the closely agreeing results calculate the percentage of the pure acid in the sample.

Illustration.—Two 1 Gm. portions of oxalic acid required 29.35 and 29.15 Cc. of $\frac{N}{2}$ alkali respectively; to calculate percentage of the acid in sample. The factor for oxalic acid with $\frac{N}{2}$ alkali V.S. is 0.031515 Gm. and is derived from the equation:

$$\underset{126.06}{H_2C_2O_4 \cdot 2H_2O} \ + \ \underset{2 \times 40.01}{2NaOH} \ = \ Na_2C_2O_4 \ + \ 4H_2O.$$

1 Lt. of $\frac{N}{2}$ NaOH contains 20.005 Gm., and corresponds to 31.515 Gm. of $H_2C_2O_4 \cdot 2H_2O$.

1 Cc. of the V.S. is the equivalent of 0.031515 Gm. of $H_2C_2O_4 \cdot 2H_2O$.

Since 29.2 Cc. of $\frac{N}{2}$ alkali were used for 1 Gm. of the sample, 29.2×0.031515 Gm. $= 0.920138$ Gm. of oxalic acid, and by proportion:

$$1 : 0.920138 :: 100 : x.$$

$$x = \frac{0.920138 \times 100}{1} = 92.0 + \text{ per cent.}$$

The sample is found to contain 92.0 + per cent. of oxalic acid.

Observation.—When the sample of an organic acid is free from CO_2 its solution need not be boiled, but the water used for solution and dilution must be free from CO_2. From water, this gas is removed by boiling and passing a current of CO_2-free air through it. Should the standard alkali V.S. contain carbonate, correct results can

be secured only by carrying out the titration in a boiling solution. This method of titration is illustrated in the standardization of ·N alkali V.S. by potassium bitartrate or of oxalic acid with alkali V.S., q. v. Evidently, volatile acids can not be titrated in boiling solutions. When they contain CO_2 the gas may be removed by boiling under a return condenser or the titration is made residual, the excess of standard alkali being titrated in hot solution with standard acid.

28. DETERMINATION OF OLEIC ACID. ($C_{18}H_{34}O_2$.)

Volumetric solutions required: $\frac{N}{10}$ Na_2CO_3 and $\frac{N}{10}$ H_2SO_4.
Indicator: Methyl orange.

Weigh a suitable quantity of the sample (0.5 to 1.0 Gm.) into a titration flask, add the standard sodium carbonate V.S. in excess, measuring it carefully, and warm till evolution of CO_2 no longer takes place. Cool the liquid, dilute to 100 Cc., add pure NaCl to saturation, shake well and filter. Wash the precipitate with a saturated solution of NaCl until the washings cease to react with red methyl orange paper and titrate the filtrate and washings, in presence of methyl orange, to the production of reddish color. From the volume of the $\frac{N}{10}$ Na_2CO_3 V.S. consumed by the sample, calculate the percentage of oleic acid present.

1 Cc. of $\frac{N}{10}$ carbonate V.S. corresponds to 0.028234 Gm. of oleic acid.

29. DETERMINATION OF FORMALDEHYDE IN SOLUTION OF FORMALDEHYDE.

Formaldehyde is oxidized to formic acid in presence of standard alkali, the alkali in excess is titrated.

Volumetric solutions employed: N-NaOH and $\frac{N}{2}$ acid.
Indicator: Litmus solution.

Neutralize 50 Cc. of a 3 per cent. solution of hydrogen peroxide with the N alkali V.S., using a drop of litmus solution. Accurately weigh 3 Cc. of the sample into a 120-Cc. erlenmeyer flask, add from a burette 50 Cc. of N alkali, cover the flask with a small funnel and at once pour in the peroxide solution in a slow stream. After having allowed the solution to stand 15 minutes, or until the evolution of oxygen has ceased, wash the outer surface of the funnel with water so as to wash down at the same time any drops of liquid adhering to the inner surface of the flask, add the indicator and titrate the unconsumed alkali with the standard acid V.S. The end of the reaction is indicated by the change of the blue color to a distinct reddish tint brought about by a final drop of the V.S. To find the alkali consumed by the sample, divide the Cc. of $\frac{N}{2}$ acid used by 2 and subtract the quotient from 50, the number of Cc. of N alkali added; difference = Cc. of N alkali consumed. Check the results of the titration by another or more titrations and calculate the percentage of HCOH in the sample.

The factor for formaldehyde, with N alkali V.S. is 0.03002 Gm. and is found from the following equations:

$$\underset{30.02}{\mathrm{HCOH}} \;+\; \mathrm{H_2O_2} \;=\; \mathrm{HCOOH} \;+\; \mathrm{2H_2O.}$$

$$\mathrm{HCOOH} \;+\; \underset{40.01}{\mathrm{NaOH}} \;=\; \mathrm{NaCOOH} \;+\; \mathrm{H_2O.}$$
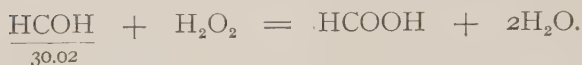
1 Lt. of N-NaOH contains 40.01 Gm., and corresponds to 30.02 Gm. of HCOH.

1 Cc. of the V.S. is the equivalent of 0.03002 Gm. of HCOH.

Therefore, by rule on page 24,

$$\frac{\text{Cc. of alkali consumed} \times 0.03002 \times 100}{\text{weight of sample}} = \text{per cent. of HCOH.}$$

Note.—Inaccuracies of this method, which is essentially that of the U.S.P., have been reported and a modification of the operation suggested by J. K. Haywood and B. H. Smith,[1] who recommend to proceed as follows:

In a suitable flask are mixed 50 Cc. of N-NaOH and 50 Cc. of pure, neutral, 3 per cent. hydrogen peroxide. By means of a pipette, 3 Cc. of the sample, specific gravity of which is carefully determined, are introduced, the tip of pipette being held close to the surface of the liquid in the flask. A small funnel is set in the neck of the flask and the flask and contents heated on water-bath during 5 minutes, mixing occasionally. Without heating, 30 minutes are required for complete oxidation. After the required time has elapsed the funnel and the neck of the flask are rinsed into the flask with water and the liquid cooled to room temperature. The unconsumed alkali is then titrated with standard acid V.S., litmus being used as indicator.

Formic acid may be titrated by the residual method of titration but is usually determined by oxidation with standard permanganate. See Chapter III.

Benzoic acid; no volumetric method available.

Salicylic acid is determined mostly colorimetrically, see Chapter V, or by precipitation, see Chapter IV.

Gallic and *Tannic acids* are determined with standard iodine or permanganate.

30. Saponification Number of Fats and Oils.
(Koettstorfer Number.)

The quantity of an alkali required to saponify, under given conditions, a definite quantity of an oil or fat was found to vary with the individual esters. When determined, this quantity is expressed as milligrams of KOH required to saponify 1 Gm. of the fat, and this expression constitutes the saponification number.

Volumetric solutions required: $\frac{N}{2}$ alcoholic potassium hydroxide and $\frac{N}{2}$ hydrochloric acid.

Indicator: Phenolphthalein solution.

[1] J. A. Chem. Soc., 1905, 27, p. 1138.

The purified fat is melted and, if necessary, filtered. Into a tared 200-Cc. flask 2 Cc. of the liquid fat are introduced and on cooling in a desiccator, accurately weighed. From a burette, 25 to 30 Cc. of the $\frac{N}{2}$ alcoholic alkali V.S. are carefully run in, the flask connected with a return condenser and the contents boiled during one half hour, or until saponification is completed. After cooling, the unconsumed alkali is titrated with the $\frac{N}{2}$ HCl V.S., using 0.5 Cc. of phenolphthalein solution as indicator. An exactly equal volume of the alcoholic KOH V.S. is then titrated with the $\frac{N}{2}$ HCl V.S. for the purpose of standardization. The volume of $\frac{N}{2}$ HCl consumed in titration of the unconsumed alkali in the saponification is then subtracted from the Cc. of the same V.S. used for titration of the alcoholic KOH by itself and the difference which represents the Cc. of $\frac{N}{2}$ HCl V.S. corresponding to alkali consumed by the fat serves for calculation of the number.

Since 1 Cc. of $\frac{N}{2}$ HCl V.S. is the equivalent of 0.028055 Gm. of KOH, the calculation is made as follows:

$$\frac{\text{Cc. of } \frac{N}{2} \text{ acid corresp. to KOH consumed} \times 0.028055 \times 1000}{\text{Wt. of fat taken}} = \text{K.N.}$$

31. VOLATILE FATTY ACID NUMBER. (Reichert-Meisel Number.)

Butter and certain other fats contain esters of volatile fatty acids. When saponified and the soap decomposed with an acid, the volatile acids are distilled off and are determined by titration. The number of Cc. of $\frac{N}{10}$ alkali V.S. required to neutralize the volatile fatty acids from 5 Gm. of a fat constitute the Reichert-Meisel number of the particular fat.

Saponification may be carried out by one of several methods; that of Leffmann and Beam only is here given.

Reagents Required. — Glycerol-soda solution: 5 Gm. of pure NaOH dissolved in 5 Cc. of water and mixed with 90 Cc. of pure glycerin.

Sulphuric acid: 20 Cc. of concentrated acid diluted with 100 Cc. of water.

Volumetric solution employed: $\frac{N}{10}$ barium hydroxide or $\frac{N}{10}$ NaOH, free from CO_2.

Indicator: Phenolphthalein solution.

Weigh 5 Gm. of the fat into a flask, add 20 Cc. of the glycerol-soda solution, and heat over naked flame or on an asbestos plate, mixing, if foam is seen to rise, until complete saponification is indicated by the mixture becoming entirely clear. Add to the contents of the flask 135 Cc. of recently boiled distilled water, very slowly, and carefully, to prevent foaming, introduce 5 Cc. of the sulphuric acid, drop in few pieces of pumice stone and connect the flask with a condenser for distillation. In distillation, heating should be so regulated as to collect 110 Cc. (in a graduated cylinder) within 30 minutes. The distillate is then mixed and filtered through a dry filter and 100 Cc. of the filtrate titrated with the $\frac{N}{10}$ barium hydroxide and phenolphthalein. One drop of the V.S. should

produce, when finally added, a distinct red color lasting 2 to 3 minutes.   From the volume of the $\frac{N}{10}$ V.S. consumed by 100 Cc. of the distillate the volume corresponding to 110 is found.   This is then corrected for a blank titration and the final number of Cc. of the $\frac{N}{10}$ alkali consumed to neutralize the volatile fatty acids from 5 Gm. of fat, constitute the Reichert-Meisel number of the fat treated.

Saponification is also carried out by heating with alcohol under a return condenser or by heating with strong alkali without alcohol in a pressure flask during 1 hour.

32. Determination of Acidity of Alcoholic Liquids.
(Whisky, Brandy, Rum.)

(*a*) Into a titration flask 25 Cc. of the sample are measured, diluted with water to 50 or 100 Cc., to reduce intensity of the color, and the liquid titrated with $\frac{N}{10}$ Ba(OH)$_2$ V.S., using phenolphthalein solution as indicator.   From the volume of Ba(OH)$_2$ V.S. consumed the total acidity, expressed as acetic acid, is calculated.

(*b*) *Volatile Acids.*—25 Cc. of the sample are distilled to near dryness, 25 Cc. of water added to the residue and distillation, to near dryness, repeated.   The distillate is diluted with distilled water to measure 100 Cc. and titrated in the presence of phenolphthalein, with $\frac{N}{10}$ barium hydroxide V.S.   The acidity indicated by the volume of the V.S. consumed is calculated into acetic acid.

(*c*) *Fixed Acids.*—The percentage of these in the sample is calculated from the difference in volumes of $\frac{N}{10}$ Ba(OH)$_2$ V.S. consumed in the two titrations and is expressed as tartaric acid.   Factors on p. 91.

33. Compound Ethers.

Those present in alcoholic liquids are determined by residual titration through saponification and the results expressed as ethyl-acetate.   The sample (100 Cc.) is distilled into a flask, exactly neutralized with $\frac{N}{10}$ barium hydroxide V.S. and phenolphthalein. To the neutral liquid 25 Cc. of $\frac{N}{10}$ NaOH (accurately measured) are added, and the contents boiled under return condenser during 1 hour.   On cooling, the contents of the flask which should be red-colored, are titrated with $\frac{N}{10}$ hydrochloric acid V.S.   From the volume of $\frac{N}{10}$ alkali V.S. consumed in decomposition of the esters the quantity of these present is calculated.   One (1) Cc. of $\frac{N}{10}$ NaOH V.S. corresponds to 0.00881 Gm. ethyl acetate.

If, during saponification, the red color of the contents of the flask disappears, more (10 Cc.) of the $\frac{N}{10}$ alkali V.S. must be added.

TABLES OF EQUIVALENTS (factors).*

NORMAL ACID V.S.

1. Bases.

Equivalents of 1 c.c.
of $\frac{N}{1}$ Acid V.S.

Ammonia, NH_3	0.01704	Gm.
Ammonium, NH_4	0.01805	Gm.
Ammonium carbonate, $(NH_4)_2CO_3$	0.04805	Gm.
Ammonium carbonate, U.S.P., $NH_4HCO_3 \cdot NH_4NH_2CO_2$	0.05238	Gm.
Ammonium hydroxide, NH_4OH	0.03506	Gm.
Barium carbonate, $BaCO_3$	0.098685	Gm.
Barium hydroxide, $Ba(OH)_2$	0.0857	Gm.
Calcium carbonate, $CaCO_3$	0.05005	Gm.
Calcium hydroxide, $Ca(OH)_2$	0.037055	Gm.
Calcium oxide, CaO	0.028045	Gm.
Lithium carbonate, Li_2CO_3	0.0370	Gm.
Magnesium carbonate, $MgCO_3$	0.04216	Gm.
Magnesium carbonate, U.S.P., $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$	0.048572	Gm.
Magnesium oxide, MgO	0.02016	Gm.
Nitrogen, N	0.01401	Gm.
Potassium bicarbonate, $KHCO_3$	0.10011	Gm.
Potassium carbonate, K_2CO_3	0.06910	Gm.
Potassium hydroxide, KOH	0.05611	Gm.
Sodium bicarbonate, $NaHCO_3$	0.08401	Gm.
Sodium carbonate, monohydrated, $Na_2CO_3 \cdot H_2O$	0.06201	Gm.
Sodium carbonate, anhydrous, Na_2CO_3	0.05300	Gm.
Sodium carbonate, $Na_2CO_3 \cdot + 10H_2O$	0.14310	Gm.
Sodium hydroxide, $NaOH$	0.04001	Gm.
Strontium carbonate, $SrCO_3$	0.07381	Gm.
Strontium oxide, SrO	0.05181	Gm.
Zinc oxide, ZnO	0.04085	Gm.

2. Organic Salts of the Alkalies.

Lithium benzoate, $LiC_7H_5O_2$	0.12805	Gm.
Lithium bitartrate, $LiHC_4H_4O_6$	0.15605	Gm.
Lithium citrate, $Li_3C_6H_5O_7 + 4H_2O$	0.094043	Gm.
Lithium salicylate, $LiC_7H_5O_3$	0.14405	Gm.
Potassium acetate, $KC_2H_3O_2$	0.09813	Gm.
Potassium benzoate, $KC_7H_5O_2 + 3H_2O$	0.21421	Gm.
Potassium benzoate, anhydrous, $KC_7H_5O_2$	0.16015	Gm.
Potassium bitartrate, $KHC_4H_4O_6$	0.18815	Gm.
Potassium citrate, $K_3C_6H_5O_7 + H_2O$	0.108123	Gm.
Potassium lactate, $KC_3H_5O_3$	0.12815	Gm.
Potassium salicylate, $KC_7H_5O_3$	0.17615	Gm.
Potassium sodium tartrate, $KNaC_4H_4O_6 + 4H_2O$	0.14111	Gm.
Sodium acetate, $NaC_2H_3O_2 + 3H_2O$	0.1361	Gm.
Sodium benzoate, $NaC_7H_5O_2$	0.14405	Gm.
Sodium bitartrate, $NaHC_4H_4O_6 + H_2O$	0.19007	Gm.
Sodium citrate, $Na_3C_6H_5O_7$	0.086017	Gm.
Sodium lactate, $NaC_3H_5O_3$	0.11205	Gm.
Sodium salicylate, $NaC_7H_5O_3$	0.16005	Gm.
Sodium tartrate, $Na_2C_4H_4O_6 + 2H_2O$	0.11504	Gm.

* See under "Factors," pp. 24–25, and "Observations," p. 55.

TENTH-NORMAL ACID V.S.

3. *Alkaloids.*

Drug.	Alkaloid.	Formula.	M.W.	Equiv. of 1 c.c. N/10 Acid V.S.	Required per cent. by U.S.P.	Per cent. Usually Present.
Aconite	Aconitine	$C_{34}H_{47}NO_{11}$	645.48	0.06455	0.5	0.2 – 0.8
Belladonna	Atropine	$C_{17}H_{23}NO_3$	289.24	0.02892	0.3 (leaf)	0.3 – 0.4
	(Hyoscyamine)				—0.45 (root)	0.3 – 1.0
	(Hyoscine)		(combined mydriatic)			
Cinchona	Quinine	$C_{20}H_{24}N_2O_2+3H_2O$	378.32	0.03783	5.0 total	4.0 –12.0
	(Quinidine)	Anhydrous	—324.26	0.03243	4.0 Eth. Sol.	
	Cinchonine	$C_{19}H_{22}N_2O$	294.24	0.02942		
	(Cinchonidine)					
Cinchona rubra	"	"	"	"	5.0 total	4.0 –10.0
Coca	Cocaine	$C_{17}H_{21}NO_4$	303.22	0.03032	0.5 "	0.4 – 0.8
	(Ecgonine), etc.					
Colchicum	Colchicine	$C_{22}H_{25}NO_6$	399.26	0.03993	0.35 (corm)	0.3 – 0.5
					—0.45 (seed)	0.4 – 0.6
Conium	Coniine (Liq.)	$C_8H_{17}N$	127.18	0.01272	0.5	0.5 – 1.5
Gelsemium	Gelsemine	$C_{22}H_{26}N_2O_3$	366.28	0.03663	—	0.2 – 0.5
	(Gelseminine)					
Hydrastis	Hydrastine	$C_{21}H_{21}NO_6$	383.22	0.03832	2.5	2.0 – 3.0
	Berberine	$C_{20}H_{17}NO_4$	335.28	0.03353	—	3.0 – 4.0
Hyoscyamus	Hyoscyamine	$C_{17}H_{23}NO_3$	289.24	0.02892	0.08 Mydr.	0.05–0.15
	(Hyoscine), etc.					
Ipecac	Emetine	$C_{15}H_{21}NO_2$	247.22	0.02472	1.75 total	1.3 – 2.5
	Cephaeline	$C_{14}H_{19}NO_2$	233.20	0.02332	—	0.4 – 0.5
Nux Vomica	Strychnine	$C_{21}H_{22}N_2O_2$	334.24	0.03342	1.25	0.7 – 1.5
	Brucine	$C_{23}H_{26}N_2O_4+4H_2O$	466.36	0.04664	—	0.8 – 1.7
Opium	Morphine	$C_{17}H_{19}NO_3+4H_2O$	303.22	0.03032	9.0	1.0 –25.0
	" anhydrous		285.20	0.02852		
Opium { powdered / deodorized / granulated }	Morphine	"	"	"	12.0 to 12.5	"
Physostigma	Physostigmine	$C_{15}H_{21}N_3O_2$	275.24	0.02752	0.15	0.1 – 0.2
Pilocarpus	Pilocarpine	$C_{11}H_{16}N_2O_2$	208.18	0.02082	0.5	0.5 – 1.0
Scoparius	Sparteine (Liq.)	$C_{15}H_{26}N_2$	234.28	0.01171	—	0.03
Scopola	Scopolamine	$C_{17}H_{21}NO_4$	303.22	0.03032	0.5 Mydr. A.	0.5 – 1.0
	(Atropine)					
	(Hyoscyamine)		(combined mydriatic) see above			
Stramonium	Daturine	$C_{17}H_{23}NO_3$	289.24	0.02892	0.35 Mydr. A.	0.2 – 0.4
	(Atropine)					
	(Hyoscyamine)	see above				

4. *Acids.*

Equivalent of 1 Cc.
of $\frac{N}{1}$ Alkali V.S.

Acetic, $HC_2H_3O_2$	0.06004	Gm.
Ammoniated mercury, NH_2HgCl	0.0125745	Gm.
Boric, H_3BO_3	0.06203	Gm.
Carbonic (anhydride) CO_2	0.02200	Gm.
Citric, $H_3C_6H_5O_7 + H_2O$	0.070033	Gm.
Formic acid, $HCOOH$	0.04602	Gm.
Hydriodic, HI	0.12793	Gm.
Hydrobromic, HBr	0.08093	Gm.
Hydrochloric, HCl	0.03647	Gm.
Hydrofluoric, HF	0.02001	Gm.
Hydrofluosilicic, H_2SiF_6	0.07216	Gm.
Hypophosphorous, HPH_2O_2	0.06603	Gm.
Lactic, $HC_3H_5O_3$	0.09006	Gm.
Nitric, HNO_3	0.06302	Gm.
Oleic, $HC_{18}H_{33}O_2$	0.28234	Gm.
Oxalic, $H_2C_2O_4 + 2H_2O$	0.06303	Gm.
Phosphoric, $H_3PO_4 =$ phenolphthalein	0.049015	Gm.
Phosphoric, $H_3PO_4 =$ methyl orange	0.09803	Gm.
Potassium dichromate, $K_2Cr_2O_7$	0.1472	Gm.
Potassium bitartrate, $KHC_4H_4O_6$	0.18815	Gm.
Sulphuric, H_2SO_4	0.049045	Gm.
Sulphurous, H_2SO_3	0.041045	Gm.
Tartaric, $H_2C_4H_4O_6$	0.07503	Gm.
Trichloracetic, CCl_3COOH	0.16339	Gm.
Formaldehyde, $HCOH$	0.03002	Gm.

CHAPTER III.

DETERMINATIONS BY OXIDATION AND REDUCTION.

General Principles.—If the terms " oxidation " and " reduction " are understood to mean changes in valence of certain elements present in the compounds which undergo these changes, then when the valence of an element is increased *oxidation* takes place while the reverse change, involving the decrease in valence, is known as *reduction*. This change in valence which is said to depend on the number of positive or negative charges of electricity an element carries, can be brought about only by the corresponding reverse change in valence of another element; both oxidation and reduction changes taking place simultaneously. In order to distinguish between oxidation and reduction in analysis, the meaning of these terms refers to changes of valence which only the elements in the substances determined undergo.

The reagents which are capable of changing valence from a lower to a higher value are called oxidizing agents; reducing agents being those reagents which change valence from a higher to a lower value. Since the oxidizing or reducing power of these reagents can be measured, it is evident that reducible and oxidizable substances may be determined volumetrically, if these reagents are employed in standard solutions. As in other titrations, standard V.S. of the reagents are added to a weighed quantity of the sample in portions until the end-reaction shows that the titration is completed. From the volume of the standard V.S. consumed the percentage of the particular substance determined is then readily calculated. Most of these reactions are oxidation reactions. Oxidation changes are brought about by two kinds of reagents, viz.: the *direct* and the *indirect* oxidizing agents.

The Reactions.—When a reagent, employed in a standard solution, itself furnishes the active oxygen by which change in valence is produced, direct oxidation takes place. In the equation:

1. $$2FeSO_4 + H_2O_2 + H_2SO_4 = Fe_2(SO_4)_3 + 2H_2O$$

is represented the direct oxidation of two molecules of ferrous sulphate by one molecule of hydrogen peroxide, the valence of Fe being changed in the process. The value of a direct oxidizing agent depends on the available oxygen it contains or rather on the work this oxygen can perform. This very important consideration must be kept clearly in mind when proper factors for calculations are to be derived from equations representing the various reactions. The above equation shows that 2 Fe(ous) are changed to 2 Fe(ic) by one H_2O_2 which contains one available oxygen.

The oxidation of sulphurous acid to sulphuric, by iodine, is represented in another equation:

2.
$$H_2SO_3 + I_2 + H_2O = H_2SO_4 + 2HI.$$
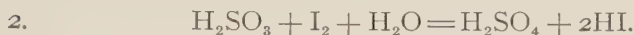
Two atoms of iodine oxidize one molecule of sulphurous acid to sulphuric. The oxidation is indirect, the iodine itself not combining with the sulphur of sulphurous acid whose valence is increased in the process, but acting on a molecule of water the oxygen of which thus becomes available. The iodine forms HI and the sulphur is changed from 4-valent to 6-valent. The value of the indirect oxidizing agents depends on the quantity of oxygen which is made available by them.

End-Reactions.—Some V.S. used in these titrations being colored and changing their color when reacting, no indicator is required in titrations performed with them. When an indicator is used in solution it reacts with a minute excess of one of the reacting substances as in the neutralization reactions. Should an indicator be found to react with both these substances, *e. g.,* the substance to be determined and the reagent in V.S., it could not be employed in the titrated liquid. In that case the end-reaction is made to take place outside the titration vessel, the drop method being resorted to. When, in a titration, the end-reaction depends on a distinct shade of color it is of advantage to prepare and use permanent standard color tints and titrate to the point where the color of the end-reaction matches the particular color tint. If desired, a correction for the reagent required to produce a distinct tint may be established and applied.

Volumetric Solutions.—Both normal and empirical V.S. are employed. The strength of the normal solutions is here based, as has been stated, on the number and valence of the atoms of an active element in a molecule of the reagent. For each unit of valency of the active element an equivalent quantity of the reagent in gms., or a simple fraction thereof, is taken and dissolved to measure 1 Lt. By definition, one liter of a normal V.S. must contain of a reagent that quantity in grammes which is the equivalent of 8 Gm. of oxygen and, therefore, corresponds to the unit of valence of its active element. In the neutralization reactions this quantity is determined by the number of replaceable hydrogens (H) or hydroxyls (OH); in the oxidation and reduction reactions, this value depends on the units of the elemental valence affected in the reaction and is measured by the oxygen furnished or consumed. Thus 1000 Cc. of N-V.S. of any reagent used in oxidation or reduction methods would have to give up or consume in reactions, 8 Gm. of oxygen. Of iodine the N-V.S. would have to contain, in 1000 Cc., that quantity of this element which corresponds to 8 Gm. of oxygen. From the equation representing the reaction of iodine and sulphurous acid this quantity is found to be 126.97 Gm., seeing that $2I (2 \times 126.97)$ make available 16 Gm. of oxygen.

A standard V.S. here may have more than one value as is well illustrated in the case of $\frac{N}{10}$ potassium dichromate V.S., *q. v.* The

value of such solution is based entirely on the function of the reagent it contains when used in any particular reaction.

INDICATORS.

In these processes the indicators employed are not numerous and are dispensed with wherever possible. Among those that are used are:

Starch Solution.—To prepare a small quantity of this solution, 0.5 Gm. of powdered starch is rubbed with a little cold water to form a thin paste and this is then poured into 100 Cc. of boiling water. The mixture is gently boiled during 2 minutes and after cooling to room temperature the solution is filtered for use. Exposed to air, starch solution is decomposed more or less rapidly. To keep it, the solution must be sterilized and kept in preferably small, well-stoppered bottles, one holding 30 to 50 Cc. Unless thus kept the solution should be made fresh when wanted. Commercial "soluble starch," dissolved in cold water, gives a good solution for this purpose. The value of starch solution as indicator in iodometric determinations depends on the production with iodine of a blue-colored compound. With very small quantities of iodine a pink color is produced. The blue compound is a weak combination and is readily decomposed by all reagents which react with iodine, the blue color being discharged in the reaction. For the end-point the production of the blue color is more rapid and easier of detection than the discharge of it; titrations should therefore be carried out in that order whenever possible. Starch solution is sensitive only when it acts in the presence of a soluble iodide and in the cold.

As an indicator for iodine, several of the volatile solvents which dissolve this element with the characteristic violet color are admirably suited, and are being now more extensively employed. Of these benzene has especially been commended. Titration with benzene as indicator must be made in well-stoppered glass vessels with glass or paraffined cork stoppers to allow thorough mixing (which is absolutely necessary), without loss. See standardization of sodium thiosulphate by permanganate.

Silver Nitrate Solution.—The reagent solution (5 per cent.) is suitable for this purpose.

Potassium Ferricyanide.—The pure salt, free from ferrocyanide, is dissolved in 10 parts of distilled water when required.

VOLUMETRIC SOLUTIONS.

PREPARATION AND STANDARDIZATION.

Preparation of Pure Potassium Dichromate $(K_2Cr_2O_7)$.—Prepare a saturated solution of the crystalline salt in boiling distilled water, filter the solution while hot and stir the cooling filtrate rapidly. Decant the cold mother liquor, wash the crystals by decantation with small portions of cold water, redissolve them in sufficient volume of hot water to make a saturated solution and cool this, stirring rapidly. Repeat the crystallization until the salt is suffi-

ciently pure to be used as a source of standard volumetric solutions. The number of recrystallizations to be made will depend entirely on the purity of the sample used. Before drying, the fine crystals should be tested for calcium, sulphates and chlorides employing for each test 0.5 Gm. of the dichromate dissolved in 10 Cc. of water. In the absence of these impurities, transfer the crystals to a smooth plain filter, wash with small portions of cold water to remove the adhering solution, allow to drain and dry, protected from dust. When thus dried, powder the crystals in a clean porcelain mortar and complete the drying, away from dust, at 120° C., to constant weight. Keep the product in a well-stoppered bottle.

Preparation of Pure Arsenic Trioxide (As_2O_3).—Arsenous acid free from sulphide is sublimed directly. When the acid contains sulphide it should be crystallized from HCl solutions to remove it. Dissolve a suitable quantity (about 10 Gm.) of the sample in just enough hot diluted HCl 1–2, filter the solution while hot and cool the filtrate to crystallize the As_2O_3. Wash the crystals several times with cold, distilled water and dry them in an evaporating dish on water-bath. Sublime the acid by heating the dish on a sandbath covered with a suitable vessel for deposition of the crystals and allow the sublimate to remain in a desiccator with $CaCl_2$ during twelve hours. Transfer to a clean bottle for storing.

Preparation of Ammonium Triiodate $((NH_4)H_2(IO_3)_3)$.—Dissolve 100 Gm. of pure iodic acid (HIO_3) in 200 Cc. of hot water, filter, add 10 Gm. of pure NH_4Cl or 3 Gm. of NH_3 as ammonium hydroxide and let stand 24 hours. Drain the crystals and recrystallize from a solution in 4 times the quantity of hot water by cooling the hot solution. Dry the crystals at 100° C. to constant weight.

$$\underset{544.83}{(NH_4)H_2(IO_3)_3} \; + \; 15KI \; + \; 16HCl$$
$$= \; \underset{9 \times 253.84}{9I_2} \; + \; 15KCl \; + \; NH_4Cl \; + \; 9H_2O.$$
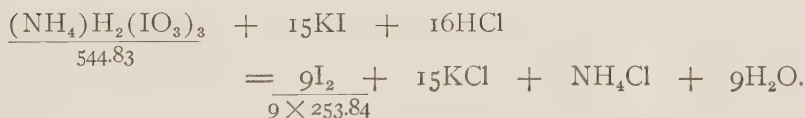
One molecule gives, with excess of KI, 9 of iodine, therefore 3.027 Gm. per liter of $\frac{N}{10}$ V.S. are required. It acts as an acid, neutralizing alkalies, and can be employed for their standardization. Luteol is the best indicator. The titration of an alkali may be performed residually, an excess of the triiodate being added, and the excess titrated with $\frac{N}{10}$ thiosulphate V.S. in presence of KI.

Tenth-normal Potassium Permanganate V.S.
1000 Cc. contain 3.1606 Gm. of $K_2Mn_2O_8$.

Prepare a stronger than tenth-normal solution by dissolving 3.3 Gm. of the crystalline salt in 1 Lt. of distilled water. Set the solution aside for 7 to 14 days, or, boil it at once during 5 to 10 minutes and then set aside for 24 hours in which time the suspended impurities will deposit. For immediate use, the boiled solution can be filtered through previously ignited asbestos, otherwise the solution, after standing during the specified length of time, is decanted

or syphoned for standardization. The water used for dilution of this solution to $\frac{N}{10}$ strength should be distilled from permanganate. For 1 Lt. of water 1 Gm. of permanganate should be used. In place of water, distilled from permanganate, it is better to employ for dilution another solution of the reagent weaker than $\frac{N}{10}$ which should be prepared in the same manner given for the stronger solution. The weaker solution is then standardized by the same method used for the stronger V.S. and the two are mixed in the proper proportions to produce the $\frac{N}{10}$ V.S.

Standardization with $\frac{N}{10}$ Oxalic Acid V.S.—Measure from a burette or by means of a pipette exactly 25 Cc. of the $\frac{N}{10}$ oxalic acid V.S. (see Chapter II) into a titration flask, add to it 5 Cc. of pure diluted sulphuric acid 1–2, then enough warm distilled water to measure 100 Cc. and titrate the liquid with the stronger permanganate solution. Add the solution from an all-glass burette in small portions, mixing contents well especially if the initial reaction is slow and the reddish color which is produced, persists. As soon as the reaction is well started the permanganate added is rapidly decolorized until the end of the reaction is approached. When the pink color of the titrated liquid produced by small portions of the V.S. begins to disappear less rapidly, reduce the flow of the V.S. to drops and continue to add it slowly, drop by drop, until a permanent pink color is imparted to the titrated liquid by one drop of the V.S. The pink color should last at least 30 seconds. The average of the volumes of permanganate consumed, in at least two closely agreeing titrations, is then found and the volume of water or of a weaker solution required for dilution is calculated.

The reaction of permanganate with oxalic acid is represented:

$$\underset{316.06}{K_2Mn_2O_8} \; + \; \underset{5 \times 126.06}{5H_2C_2O_4 \cdot 2H_2O} \; + \; 3H_2SO_4$$
$$= \; K_2SO_4 \; + \; 2MnSO_4 \; + \; 10CO_2 \; + \; 10H_2O.$$
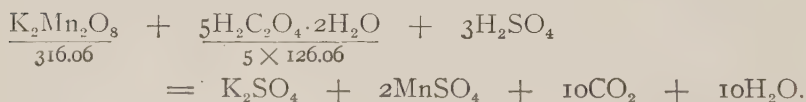
One molecule of potassium permanganate (316.06) furnishes 5 atoms of active oxygen (5×16) which decompose 5 molecules of the oxalic acid (5×126.06). Now, one molecule of the acid was found to react with 2 molecules of NaOH (see p. 53). The 5 molecules of oxalic acid decomposed by one of the permanganate will then react with 10 NaOH, therefore, one molecule of permanganate corresponds to 10 molecules of NaOH or $\frac{1}{10}$ of it corresponds to 1 NaOH. Further, since one molecule of permanganate gives up 5 active oxygens, its equivalent of 8 Gm. of oxygen is $\frac{1}{10}$ of the quantity represented by its molecular weight in grammes, or 31.606 Gm. This quantity would then have to be present in 1 Lt. of its normal V.S. For the tenth-normal V.S. the quantity of the pure salt in 1000 Cc. will, therefore, be 3.1606 Gm., or the equivalent of 0.8 Gm. of oxygen.

Illustration.—Three portions of $\frac{N}{10}$ oxalic acid, of 25 Cc. each, required 22.6, 22.4 and 22.5 Cc. of a stronger than $\frac{N}{10}$ permanganate solution; to dilute the solution to the tenth-normal strength.

Since an average of 22.5 Cc. of the stronger solution has been required for 25 Cc. of the $\frac{N}{10}$ oxalic acid the 22.5 Cc. of permanganate must be diluted with 2.5 Cc. of water, both being measured at standard temperature. But if a weaker than $\frac{N}{10}$ V.S. of the reagent be also had of which, by titration, 28.2 Cc. are required to decompose 25 Cc. of $\frac{N}{10}$ oxalic acid, then the weaker solution contains in 28.2 Cc., 3.2 Cc. of water in excess. If, then, one solution has an excess of 3.2 Cc. of water in 28.2 Cc. and the other needs 2.5 Cc. of water for dilution of 22.5 Cc. of it, the proportion in which they are to be mixed is found:

$$22.5 \times 3.2 = 72.0 \text{ volumes of the stronger solution.}$$

$$28.2 \times 2.5 = 70.5 \text{ volumes of the weaker solution.}$$

After proper dilution in either case a check titration with 40 to 50 Cc. of $\frac{N}{10}$ oxalic acid should be carried out and any necessary correction carefully made.

Crystalline, pure sodium oxalate has of late been introduced (Soerensen) and found a valuable source of standard permanganate and also of the V.S. used for neutralization processes.

Standardization with Metallic Iron.—Clean a piece of pure iron wire with emery paper, then with a clean cloth, wind it into a spiral and, cutting it into sections of about 0.1 to 0.2 Gm., weigh two or three of them very accurately. In a 100 Cc.-flask the stopper of which is provided with a " Bunsen valve," Fig. 30, boil 50 Cc. of 10 per cent. sulphuric acid, drop in a small quantity (0.1 Gm.) of Na_2CO_3 and as soon as the effervescence has nearly ceased introduce 0.1 to 0.2 Gm. of the wire and at once stopper the flask with the valve stopper. Place on water-bath and heat until the wire is all dissolved, then heat on wire gauze to boiling. Add to the hot solution 20 Cc. of 10 per cent. sulphuric acid and titrate at once with the stronger permanganate. In the titration, which is performed in the

FIG. 30. STOP-PER WITH " BUNSEN VALVE."

manner given in the method with oxalic acid, one final drop of the V.S. should produce a permanent pink color lasting 30 seconds. Repeat the operation with another or several portions of the wire for a close average. Then carry out a blank titration under like conditions in which as much of the dilute sulphuric acid and sodium carbonate should be used as in the determination. The volume of permanganate consumed in the blank is to be subtracted from that required for the iron solution. From the difference, which represents the volume of V.S. consumed by the iron, calculate the volume of water required for dilution to $\frac{N}{10}$ strength. The reactions involved in this standardization are represented:

8

a. $\underset{55.85}{\underline{Fe}}$ + H_2SO_4 = $FeSO_4$ + H_2.

b. $\underset{10 \times 55.85\,(Fe)}{\underline{10FeSO_4}}$ + $\underset{316.06}{\underline{K_2Mn_2O_8}}$ + $8H_2SO_4$

$\qquad$ = $5Fe_2(SO_4)_3$ + K_2SO_4 + $2MnSO_4$ + $8H_2O$.

It will be seen that 10×55.85 Gm. or 558.5 Gm. of Fe as ferrous salt require 316.06 Gm. of permanganate for oxidation to the ferric state.

1 Lt. $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 5.585 Gm. of iron. In order to find the volume of water required for dilution it is necessary to calculate the volume of $\frac{N}{10}$ permanganate a given quantity of pure iron would require for oxidation.

Illustration.—If, for example, 0.16 Gm. of Fe wire were used in the standardization and required 25.8 Cc. of the stronger permanganate solution, then the volume of $\frac{N}{10}$ permanganate this stronger solution would consume, or is equal to, is obtained:

$$5.585 : 1000 :: 0.16 : x.$$

$$x = \frac{1000 \times 0.16}{5.585} = 28.64 \text{ Cc.},$$

which, if the Fe was found to be only 99.5 per cent. pure, will be 28.5 Cc.

Therefore, each 25.8 Cc. of the stronger permanganate must be diluted to 28.5 Cc. at standard temperature and will require 2.7 Cc. of water.

Remarks.—The iron wire though it may be very pure contains some impurities. The exact proportion of the impurity of a larger quantity of the wire is usually established by gravimetric determination and the correction found is then properly applied, whenever the wire is used for titration. The best piano wire is from 99.5 to 99.9 per cent. pure. Electrolytic iron has been used in place of the wire with success, but the process of its preparation makes the method of standardization ill adapted to frequent needs.

The " Bunsen valve " is a simple device for protection of the ferrous salt against oxidation. It allows the hydrogen, generated in the reaction and other gases, to leave the flask through the slit (c) in the rubber tube while the outside air pressing the rubber surfaces together can not enter. Sodium carbonate reacting with the acid gives off CO_2 which displaces the air above the acid and leaves the space filled with CO_2. The use of the carbonate may be dispensed with by passing a current of CO_2 through the solution during the reaction of the acid and Fe.

If it is to be used for determination of iron and its salts, the stronger solution of permanganate need not be diluted to $\frac{N}{10}$ strength, the quantity of Fe represented by one (1) Cc. of it being found and used as the factor. The standard potassium permanganate

V.S. should be kept in clean, glass-stoppered bottles away from direct sunlight.   Only all-glass burettes are to be used in titrations with it.   Burettes or other vessels which contained permanganate, and are soiled by it, may be readily cleaned with a little oxalic acid or hydrogen peroxide solution, these reagents being removed by washing with water, subsequently.   Though potassium permanganate is readily decomposed by reducing agents, especially organic matters, its solutions, when properly prepared and kept, retain their strength remarkably well, remaining unaltered often longer than a year.

Standardization with $\frac{N}{10}$ Sodium Thiosulphate V.S.—Acidify 10 Cc. of 10 per cent. solution of KI, free from iodate, with 10 Cc. of 10 per cent. of pure sulphuric acid, dilute the solution to 150 or 200 Cc. and slowly run in, from a burette, 20 Cc. of the stronger permanganate solution in portions, mixing well between the successive additions.   Titrate the liberated iodine with $\frac{N}{10}$ thiosulphate V.S. so that one drop of the V.S. will just discharge the final yellow color of the titrated liquid.   Having checked the results by repeated titrations, calculate the volume of water or of a weaker solution of permanganate required for dilution to tenth-normal strength.   Each 20 Cc. of the permanganate solution are to be diluted to exactly equal the volume of $\frac{N}{10}$ thiosulphate consumed in titration of the iodine liberated.   The two reactions are represented:

$$K_2Mn_2O_8 + 10KI + 8H_2SO_4 = 10I + 2MnSO_4 + 6K_2SO_4 + 8H_2O.$$
$$10I + 10Na_2S_2O_3 \cdot 5H_2O = 10NaI + 5Na_2S_4O_6 + 5H_2O.$$
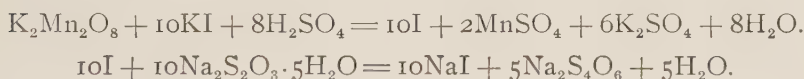
Note.—This method of standardization is not commonly employed. It is essentially the reverse of the standardization of sodium thiosulphate V.S. with $\frac{N}{10}$ potassium permanganate V.S.   The titration may be made residual, starch solution being used as indicator.   For this purpose standard iodine V.S. of exact strength is used in addition to the thiosulphate.   The $\frac{N}{10}$ thiosulphate is added until the iodine liberated by permanganate is all combined and the excess of it is titrated with the standard iodine V.S., added until a blue color is produced by one drop of the V.S., starch being used as indicator.

TENTH-NORMAL POTASSIUM DICHROMATE V.S.

1000 Cc. contain 4.9066 + Gm. of $K_2Cr_2O_7$.

Accurately weigh 4.9067 Gm. of the pure, dry potassium dichromate (see p. 94) into a carefully calibrated 1-Lt. flask, dissolve in distilled water and dilute the solution to measure, at standard temperature, exactly 1000 Cc.   The volumetric solution thus prepared needs no further standardization.   Should the purity of the reagent be questioned, the solution may be standardized by titration with $\frac{N}{10}$ NaOH V.S., using phenolphthalein.   It should be noted that $\frac{N}{10}$ dichromate V.S. used as an oxidizing agent differs from $\frac{N}{10}$ dichromate when employed to neutralize bases.   With the exception of the standard acid and alkali V. Solutions this $\frac{N}{10}$ dichromate equals all the other

tenth-normal V. Solutions. With $\frac{N}{10}$ alkalies this solution is only one third tenth-normal, 3 Cc. of it being required to neutralize 1 Cc. of $\frac{N}{10}$ alkali V.S.   This dual value of the $\frac{N}{10}$ dichromate depends entirely on the function performed by the reagent in different reactions.   This may be illustrated by the following equations:

1. $\underset{294.4}{K_2Cr_2O_7}$ $+$ $2KOH$ $=$ $2K_2Cr_2O_7.$

2. $\underset{294.4}{K_2Cr_2O_7}$ $+$ $6FeSO_4$ $+$ $8H_2SO_4$

   $=$ $3Fe_2(SO_4)_3 +$ $2KHSO_4$ $+$ $Cr_2(SO_4)_3$ $+$ $7H_2O.$
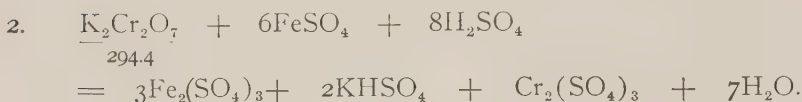
Reacting with bases, one (1) molecule of the dichromate is dibasic and, therefore, equals 2 units of valence, or acts as a dibasic acid.

With oxidizable substances (eq. 2) one molecule furnishes 3 atoms of active oxygen which are equal to 6 units of valence.   In any normal solution, the quantity of the reagent in 1000 Cc. corresponds to one unit of valence of the active element in its molecule. Since this $\frac{N}{10}$ V.S. of dichromate is employed as an oxidizing agent the quantity of it which must be present in 1 Lt. of $\frac{N}{10}$ solution will be derived from equation 2.   Further, since 1000 Cc. of the $\frac{N}{10}$ V.S. must contain, of the reagent, 0.1 of the equivalent of 8 Gm. of oxygen, and the equivalent of dichromate is $\frac{294.4}{6} = 49.066 +$ Gm.,

1 Lt. of the $\frac{N}{10}$ V.S. must, therefore, contain $\frac{49.066}{10} +$ or $4.9066 +$ Gm. of the pure salt.   When this V.S. is used to neutralize bases it has the value of $\frac{N}{30}$.   Should it be desired to prepare a tenth-normal V.S. of the dichromate to be used in neutralization reactions, its strength would have to be based on the reaction represented in equation 1, and 1 Lt. of the solution would have to contain $\frac{294.4}{20}$ $= 14.72$ Gm. of the pure salt.   The value of this solution, when used for oxidation, would be $\frac{3N}{10}$.

Note.—Used for standardization of sodium thiosulphate V.S. $\frac{N}{10}$ dichromate V.S. gives slightly high results due to the catalytic action of the chromium salts produced.

A correction for this action has been devised by using a lower atomic weight of chromium.   Except for especially accurate results, no correction is needed.

Tenth-normal Oxalic Acid V.S.

1000 Cc. contain 6.303 Gm. of $H_2C_2O_4 \cdot 2H_2O$.

For preparation and standardization of this V.S. see neutralization methods, page 53.   Standard oxalic acid readily deteriorates on keeping.   To overcome or minimize this tendency, Riegler has proposed the addition of 50 Cc. of pure, concentrated sulphuric acid

to each liter of the $\frac{N}{10}$ V.S. This addition is, of course, permissible only to oxalic acid used for oxidation processes and must be made before the stronger oxalic acid, prepared for standardization, is diluted to the $\frac{N}{10}$ strength. The advantageousness of this addition has been recently confirmed.

TENTH-NORMAL SODIUM THIOSULPHATE V.S.

1000 Cc. contain 24.824 Gm. of Na₂S₂O₃·5H₂O.

Prepare a stronger than $\frac{N}{10}$ solution by dissolving 30 Gm. of the crystalline salt which should be free from calcium, free alkalies, sulphates and chlorides, in 1000 Cc. of cold, recently boiled distilled water, and standardize the solution by titration and subsequent dilution.

Standardization with $\frac{N}{10}$ Potassium Dichromate V.S. — In a ½-liter flask dissolve 1 Gm. of KI, free from iodate, in a small volume of pure 10 per cent. sulphuric acid. From a burette, run into this solution 20 to 25 Cc., accurately measured, $\frac{N}{10}$ potassium dichromate V.S. in a slow stream, mixing the contents well. When the V.S. has all been added, close the flask and let stand 5 to 10 minutes, then dilute the liquid to about 250 Cc. with distilled water and titrate it with the stronger thiosulphate solution. Add the thiosulphate in small portions (0.5 Cc.), mixing well, until the yellow color, due to a small quantity of iodine is barely, yet distinctly, recognizable in the titrated liquid which itself is of light green color. When this point has been reached, add 2 Cc. of starch solution and complete the titration by the addition of the V.S., a drop at a time, mixing well after each addition, and increasing the time between them. The deep blue color of iodized starch should be finally changed to light green color of the chromium salt by one drop of the V.S. From an average of the results of several agreeing titrations the volume of water required for dilution to $\frac{N}{10}$ strength is calculated.

Illustration.—If, for example, the average of three titrations, performed in the manner described, is found to be 23.4 Cc. of thiosulphate required to react with the iodine set free by 25 Cc. of $\frac{N}{10}$ dichromate, then the addition of 1.6 Cc. of recently boiled, distilled water to every 23.4 Cc. must be made. The solution and water are to be both at standard temperature. The $\frac{N}{10}$ sodium thiosulphate V.S. thus produced, should then be checked by titrating with it a larger volume of the $\frac{N}{10}$ dichromate. The reactions involved are represented:

$$6KI + \underset{294.4}{\underline{K_2Cr_2O_7}} + 7H_2SO_4 = 4K_2SO_4 + Cr_2(SO_4)_3 + 3I_2 + 7H_2O.$$

$$3I_2 + \underset{6 \times 248.24}{\underline{6Na_2S_2O_3 \cdot 5H_2O}} = 3Na_2S_4O_6 + 6NaI.$$
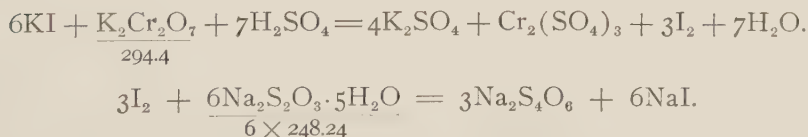
One molecule of potassium dichromate (294.4) contains 3 active oxygens which liberate 6 atoms of iodine and these in turn react

with 6 molecules of sodium thiosulphate (6×248.24). One molecule of the thiosulphate therefore corresponds to one unit of valence. Since $4.9066 +$ Gm. is the quantity of potassium dichromate present in 1000 Cc. of its $\frac{N}{10}$ V.S., and this quantity is the equivalent of 0.8 Gm. of oxygen or of 12.692 Gm. of iodine, then the quantity of sodium thiosulphate which corresponds to this equivalent must, therefore, be 24.824 Gm. Standard sodium thiosulphate V.S. is used exclusively in titrations of iodine. The salt used for the V.S. should be very pure; it is readily purified by recrystallization and should then be dried at 90° to 100° C.

The standardized V.S. is to be kept in clean, glass-stoppered bottles. Though regarded very perishable, the solution, when prepared from pure materials, keeps well. Acids, even CO_2, act upon it causing it to become weaker, hence the necessity to employ recently boiled, distilled water in its preparation. On long standing (6 months or longer) the solution deteriorates and requires restandardization by titrations. The products of the reaction of iodine and the thiosulphate are an iodide and tetrathionate, both colorless in solution, so that in the absence of other color no indicator is required in titrations, the color of iodine being visible in even very weak solutions.

Observations.—The end-point which lacks sharpness is recognized with some difficulty in a greenish-colored liquid; more so, because the change from blue to colorless is slow. This may be partly corrected by completing the titration with standard iodine V.S. which need not be $\frac{N}{10}$ but whose exact relation with the stronger thiosulphate must be established. In this titration the stronger thiosulphate is added in excess and the excess titrated with the standard iodine, using starch solution as indicator. One drop of the iodine V.S. should produce a distinct blue color. The volume of the stronger thiosulphate which corresponds to the volume of standard iodine V.S. consumed by the excess is to be deducted from the volume of thiosulphate added and the dilution is then made as in the direct titration. Direct titration is conveniently performed with a volatile solvent as indicator.

End-point with Chloroform as Indicator.—Employ in the titration a 200 to 250 Cc. glass-stoppered flask with a long, slender neck. Proceed as usual but, when the iodine is liberated, dilute the liquid to 100 Cc. with water, and run in the $\frac{N}{10}$ thiosulphate V.S. until the iodine color almost disappears, add 5 Cc. of chloroform and mix well by shaking. Invert the closed flask so that the chloroform layer separates in the neck of the flask where its color is observed. Iodine imparts to chloroform a violet-red color. Complete the titration by adding of the V.S., 1 to 2 drops at a time, shaking well after each addition, and observing the color of the chloroform layer. When finally one drop of the V.S. is found to have completely decolorized the chloroform, the titration is completed.

Standardization with $\frac{N}{10}$ Potassium Permanganate V.S.—Proceed as given for standardization of potassium permanganate, with $\frac{N}{10}$ thiosulphate, employing preferably the residual method. Having subtracted the volume of the permanganate which corresponds to

the standard iodine required for excess of the thiosulphate, find the volume of water required for dilution to $\frac{N}{10}$ strength. To check the strength of the $\frac{N}{10}$ solution another titration should be made in which 40 to 50 Cc. of the $\frac{N}{10}$ permanganate are used.

Standardization with $\frac{N}{10}$ Ammonium Triiodate V.S.—Dissolve 1 Gm. of pure KI in 40 Cc. of water, add 1 Cc. of pure concentrated HCl, then 10 Cc. of $\frac{N}{10}$ ammonium triiodate V.S., and titrate with the stronger sodium thiosulphate, using starch solution. The starch should be added when the iodine has been nearly all combined, which is indicated by a light yellow color. The dilution of the stronger thiosulphate is then readily made.

Standardization with Potassium Diiodate ($KH(IO_3)_2$).—Accurately weigh 0.1625 Gm. of the pure diiodate, dissolve in water, add an excess of KI (1 Gm.), then diluted HCl and, after a few minutes, titrate with the stronger thiosulphate so that the final yellow color of the solution is just discharged by one drop of the V.S.

$$\underset{389.95}{KH(IO_3)_2} + 10KI + 11HCl = \underset{12 \times 126.92}{12I} + 11KCL + 6H_2O.$$
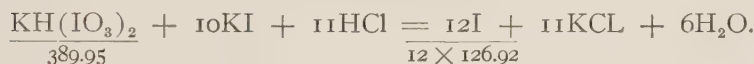
The reaction takes place independently of the excess of the acid or the dilution of the solution. The thiosulphate is then diluted so that the volume of it consumed in titration should measure, at standard temperature, exactly 50 Cc. By a trial titration another adjustment, if need be, is made. In place of the diiodate, potassium bromate may be used, the quantity of this compound, required for a titration, is found from the equation:

$$\underset{167.02}{KBrO_3} + 6KI + 3H_2SO_4 = 6I + KBr + 3K_2SO_4 + 3H_2O.$$
$$(0.0027837 \text{ Gm. is the equivalent of 1 Cc. } \tfrac{N}{10} \text{ thiosulphate.})$$
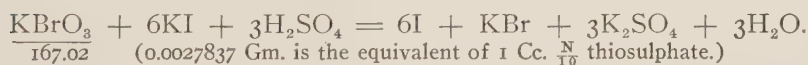
Note.—This reaction has been made use of for the standardization of acids with $\frac{N}{10}$ sodium thiosulphate. Acids reacting with an iodide and iodate, or bromate, in solution, liberate an equivalent quantity of iodine which is then found by titration with standard thiosulphate V.S. In practice 5 to 50 Gm. of the acid, according to its approximate strength and relation to the nearest normal V.S. are accurately measured into a 100-Cc. bottle provided with a glass stopper, diluted to 50 Cc. with water, 15 Cc. of 3 per cent. KIO_3 of $KBrO_3$, together with 2 Gm. KI are added and the contents allowed to stand 15 minutes. The iodine set free is then titrated with the standard thiosulphate V.S.

$$6I + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6.$$
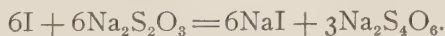
Since one molecule of sodium thiosulphate corresponds to one replaceable hydrogen of an acid, the volume to which the titrated acid must be diluted is readily found. This method is, therefore, suitable for standardization of the stronger acids.

Standardization with $\frac{N}{10}$ Silver Nitrate V.S.—Silver nitrate and a thiosulphate produce silver sulphide which precipitates.

To a measured volume of the stronger thiosulphate an excess of $\frac{N}{10}$ silver nitrate V.S. is added from a burette, the mixture boiled until the precipitate separates in flocculent form. The mixture is then made to measure a definite volume and, in aliquots of it, the silver nitrate in excess is titrated by Volhard's method (see Chapter IV.). The thiosulphate is then diluted to a volume exactly equal to that of $\frac{N}{10}$ AgNO$_3$ consumed by it.

Tenth-normal Arsenous Acid V.S.

1000 Cc. contain 4.95 Gm. of As$_2$O$_3$.

Weigh very accurately 4.95 Gm. of the sublimed arsenic trioxide, see p. 95, into a clean, carefully calibrated liter flask and dissolve it in a minimum of concentrated solution of sodium or potassium hydroxide. Prepare the alkali solution, free from iron, by dissolving 10 Gm. of the purified hydroxide in 30 Cc. of distilled water, filtering the solution through pure asbestos. When the arsenic trioxide has all dissolved, add 100 Cc. of water and saturate the solution with CO$_2$, or neutralize the excess of the alkali with pure dilute sulphuric acid, using phenolphthalein, and add a filtered solution of NaHCO$_3$, 20 Gm. in 500 Cc. of distilled water. The solution, which should not give a pink color with phenolphthalein, is then diluted to exactly 1000 Cc. at standard temperature. The quantity of As$_2$O$_3$ (4.95 Gm.) in 1 Lt. of the solution is found from an equation representing the reaction of the trioxide with oxidizing agents. With iodine, the reaction is represented:

$$\underset{198}{As_2O_3} + \underset{4 \times 126.92}{4I} + 2H_2O = As_2O_5 + 4HI.$$
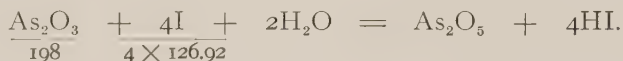
In this reaction one molecule of As$_2$O$_3$ consumes 2 atoms of oxygen made available by 4 atoms of iodine. The equivalent of 8 Gm. of oxygen is, therefore, $\frac{198}{4}$ or 49.5 Gm. of arsenic trioxide, and of 0.8 Gm. it is 4.95 Gm. The tenth-normal V.S. must, therefore, contain in 1000 Cc. 4.95 Gm. of As$_2$O$_3$. The V.S. contains an alkali bicarbonate, the As$_2$O$_3$ being present in it as an arsenite.

Tenth-normal Iodine V.S.

1000 Cc. contain 12.692 Gm. of Iodine.

Prepare a somewhat stronger than $\frac{N}{10}$ solution of sublimed iodine. To this end dissolve, in a liter flask, 20 Gm. of pure KI in a small volume of water, add to the solution 12.8 Gm. of sublimed iodine, close the flask and mix the contents by gentle shaking until the iodine is dissolved. Dilute the solution with distilled water to measure 1000 Cc. Should the solution contain suspended impurities, these may be removed by filtration through asbestos. Adjust the strength of the solution to $\frac{N}{10}$ by titration and the required dilution.

Standardization with $\frac{N}{10}$ Sodium Thiosulphate V.S.—Accurately measure into an erlenmeyer flask 25 Cc. of the iodine solution, and

carefully titrate with the $\frac{N}{10}$ thiosulphate V.S. Add the V.S. slowly, and in small portions, keeping the titrated liquid well agitated. When the brown color of the iodine solution has changed to light yellow, add of the V.S., drop at a time, mixing thoroughly, so that finally the yellow color is found discharged by one drop of the standard thiosulphate. To check the accuracy of the result carry out another or more titrations in the manner of the first and, from the average of the closely-agreeing results, calculate the volume of water to be added to change the solution to tenth-normal strength.

Illustration.—If, for example, 25 Cc. of a stronger than $\frac{N}{10}$ iodine solution required 26.8 Cc. of $\frac{N}{10}$ thiosulphate V.S as an average of three titrations, then to reduce the solution to $\frac{N}{10}$ strength, the 25 Cc. of the solution must be diluted to 26.8 Cc., or will require 1.8 Cc. of water for dilution. Therefore, for every 26.8 Cc. of the solution 1.6 Cc. of water, both being measured at standard temperature, must be added.

Standardization with $\frac{N}{10}$ Arsenous Acid V.S.—Measure exactly 25 Cc. of the iodine solution into a titration flask and titrate with $\frac{N}{10}$ arsenous acid V.S. Run the standard solution in slowly, mixing well, until the brown color of the titrated liquid has changed to light yellow. At this point add 2 Cc. of starch solution and complete the titration by adding the V.S. in drop portions and at successively longer intervals of time. When the deep blue color of the solution is changed to pink, which is permanent on mixing, the titration is completed. Carry out check titration with an equal volume of the stronger iodine solution and, from the results, calculate the volume of water required for dilution to the $\frac{N}{10}$ strength.

Observations.—In the titration with thiosulphate, iodine oxidizes the thiosulphate to tetrathionate as per equation:

$$\underset{2 \times 126.97}{2I} \quad + \quad \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} \quad = \quad 2NaI \quad + \quad Na_2S_4O_6 \quad + \quad 5H_2O.$$
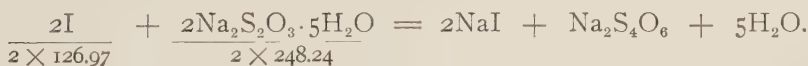
Two molecules of thiosulphate reacting with 2 iodine atoms, one iodine is found to correspond to one thiosulphate; then, since, I Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., it corresponds to 12.692 Gm. iodine,

1 Cc. of $\frac{N}{10}$ iodine will contain = 0.012692 Gm. iodine.

By definition, the equivalent of 0.8 Gm. of oxygen is 12.692 Gm. of iodine.

With arsenous acid the reaction, in which arsenic acid is formed, is represented:

$$\underset{4 \times 126.92}{4I} \quad + \quad \underset{198}{As_2O_3} \quad + \quad 2H_2O \quad = \quad As_2O_5 \quad + \quad 4HI.$$
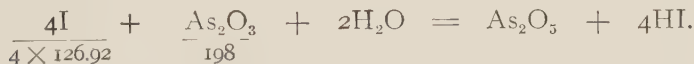
One molecule of arsenic trioxide requires 4 atoms of iodine for oxidation, and, since in 1 liter of $\frac{N}{10}$ arsenous acid solution there are 4.95 Gm., this then corresponds to 12.692 Gm. of iodine.

The reaction of iodine with arsenous acid is a reversible one, the reverse action being represented in the equation:

$$As_2O_5 + 4HI = As_2O_3 + 2H_2O + 4I.$$

Were this reaction allowed to take place, titration of iodine with arsenous acid, or vice versa, would be impossible. The reverse reaction will not take place in the absence of HI. Neutralization of the acid with a base has the effect of removing the HI, the iodide thus formed not reacting with As_2O_5. But the base used can not be a soluble hydroxide or carbonate, for these compounds themselves react with iodine; as a neutralizing agent a bicarbonate or an acid phosphate alone is suitable, though borates have also been employed.

Note.—Tenth-normal iodine V.S. may also be prepared by dissolving 12.692 Gm. of pure iodine in a solution of potassium iodide and diluting the solution to measure, at standard temperature, exactly 1000 Cc. This, apparently the simplest method, gives an exact $\frac{N}{10}$ V.S. only when an absolutely pure iodine is had. But, as the purification of the iodine for this purpose involves many difficulties, with constant uncertainty as to the purity of the product, nothing is gained by such procedure. In view of these considerations it was deemed advisable not to dwell on the process.

Volumetric solution of iodine may be also standardized by titration with pure antimony and potassium tartrate.

I. DETERMINATIONS BY DIRECT OXIDATION.

A. Titrations with Standard Potassium Permanganate V.S.

1. Determination of Hydrogen Dioxide.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

Accurately weigh about 10 Gm. of the solution of sample, dilute with water to measure exactly 100 Cc., and employ 20 Cc. portions (2 Gm. sample) for individual titrations. To 20 Cc. of the diluted solution, in a titration flask, add 5 Cc. of 10 per cent. sulphuric acid and run in the $\frac{N}{10}$ V.S. slowly, agitating the titrated liquid by rotation of the flask. When the permanganate color in the titrated solution begins to disappear slowly, add the V.S. in drop portions so that one drop will finally be found to impart, to the titrated liquid, a distinct pink color permanent 1 minute. Repeat the titration with several of the aliquots and, from the average of the results, calculate the percentage of H_2O_2 in the sample. The factor for hydrogen dioxide with $\frac{N}{10}$ V.S. is 0.001701 Gm., and is found from the equation:

$$\underset{5\times34.02}{5H_2O_2} + \underset{316.06}{K_2Mn_2O_8} + 3H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 8H_2O + \underset{5\times32}{5O_2}.$$
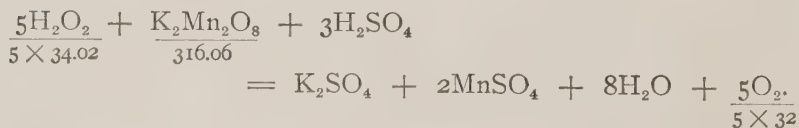
One permanganate (316.06) reacts with five hydrogen dioxide (5 × 34.02).

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 5 × 0.3402 Gm. of H_2O_2.

1 Cc. of the V.S. is the equivalent of 0.001701 Gm. of H_2O_2.
To calculate the percentage, the rule on p. 24 gives:

$$\frac{0.001701 \times \text{Cc. of } \frac{N}{10} \text{ V.S.} \times 100}{\text{weight of sample}} = \text{percentage of } H_2O_2.$$

Observations.—The 10 oxygen atoms set free are furnished equally by the two reacting substances: 5 hydrogen peroxide molecules give 5 oxygens and one permanganate also 5O. Sulphuric acid must be present to form manganese sulphate with oxides of manganese which would otherwise be precipitated and cause discoloration of the titrated liquid.

In the presence of glycerin, ether, salicylic acid and of other organic substances which decompose permanganate without reacting with the peroxide, the H_2O_2 should be determined iodometrically. For this purpose a suitable quantity of the sample is mixed with 5 Cc. of 10 per cent. sulphuric acid, 1 Gm. of KI, free from iodate, is added and the mixture allowed to stand one half hour at 25° to 30° C. After dilution of the solution with an equal volume of water, the liberated iodine is titrated with standard thiosulphate V.S.

1 Cc. of $\frac{N}{10}$ thiosulphate is the equivalent of 0.001701 Gm. H_2O_2.

Note.—To obtain readings of oxygen volumes, yielded by the solution of hydrogen dioxide, in Cc. of permanganate V.S. consumed, M. Ruliere proposed the use of an empirical V.S. of the permanganate, 1000 Cc. of which contain 5.65 Gm. of the pure salt. Since 5 atoms of oxygen correspond to one molecule of permanganate, and are also yielded by 5 molecules of hydrogen dioxide, then 5×34.02 Gm. or 170.1 Gm. of H_2O_2 will yield 80 Gm. of oxygen. One liter of oxygen, under normal conditions, weighs 1.43 Gm. and the quantity of permanganate which would liberate 1.43 Gm. of oxygen from hydrogen dioxide is

$$\frac{316.06 \times 1.43}{80} = 5.65 \text{ Gm.}$$

Using exactly one (1) Cc. of a sample of hydrogen dioxide and titrating it in the usual manner with permanganate containing 5.65 Gm. of the salt in 1 Lt., each 1 Cc. of the V.S. consumed will indicate 1 Cc. of oxygen.

When persulphates are present (not more than 0.08 Gm.), the permanganate V.S. should be rapidly added in excess and the excess determined iodometrically.

2. DETERMINATION OF SODIUM DIOXIDE.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

Weigh accurately from 0.1 to 0.2 Gm. of the sample contained in a small capsule made of the bottom part of a test tube and placed in a glass-stoppered weighing flask. Remove the capsule with metallic forceps and immerse at once in about 500 Cc. of distilled water, contained in a beaker, in such a manner that no Na_2O_2 should reach

the surface.   If, however, this should have happened, the opera-
tion must be repeated.   Acidify the solution with dilute sulphuric
acid and titrate with the permanganate V.S.

1 Cc. of the $\frac{N}{10}$ potassium permanganate V.S. is the equivalent
of 0.00390 Gm. Na_2O_2.

3. Determination of Oxalic Acid.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

Dissolve 1 Gm. of the sample in water to measure 100 Cc.   For
each titration 10 Cc. are then accurately measured into the titra-
tion flasks.   Add to 10 Cc. of the solution 10 Cc. of 10 per cent.
sulphuric acid and titrate with the $\frac{N}{10}$ permanganate.   When one
drop of the V.S. is found to have produced a distinct pink color,
permanent 1 minute, the reaction is completed.   From the results
of several titrations calculate the percentage of $H_2C_2O_4 \cdot 2H_2O$ in the
sample.   The factor for oxalic acid with $\frac{N}{10}$ V.S. is 0.006303 Gm.,
and is derived from the equation:

$$\underline{5H_2C_2O_4 \cdot 2H_2O} + \underline{K_2Mn_2O_8} + 3H_2SO_4$$
$$5 \times 126.06 \qquad \quad 316.06$$

$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 10H_2O.$$
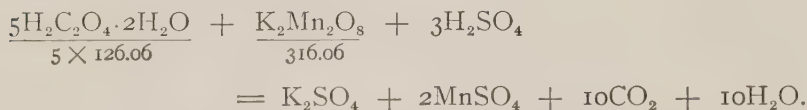
One molecule of permanganate (316.06) reacts with five of oxalic
acid (5 × 126.06).

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds
to 5 × 1.2606 Gm. oxalic acid.

1 Cc. of the V.S. is the equivalent of = 5 × 0.0012606 = 0.006303
Gm. $H_2C_2O_4 \cdot 2H_2O$.

Observations.—If, in the beginning of the titration, the titrated
liquid turns brown, the V.S. must be added more slowly and the
titrated liquid be agitated vigorously.   Should the brown color per-
sist, more sulphuric acid may be required.   The function of the
sulphuric acid is to combine manganese oxides which would other-
wise be precipitated.   In the presence of HCl, provided the quantity
of the acid is not larger than 1 Cc. of 1.04 acid in 7.5 Cc. of the
oxalic acid solution, the titration with permanganate is to be carried
out at 70° C. as recommended by Baxter and Zanetti, with good
results.

4. Determination of Calcium.

Calcium is precipitated as calcium oxalate which is then titrated.

Volumetric solution employed: $\frac{N}{10}$ potassium permanganate.

For one titration weigh accurately 0.2 to 0.3 Gm. of the sample
into a beaker, cover with 20 Cc. of water, and warm to assist solu-
tion.   In the case of the water-insoluble calcium compounds (espe-
cially the carbonate) drop in strong HCl carefully, keeping the beaker
covered, with a clock glass, as much as possible in order to prevent
loss by effervescing.   Heat the solution to boiling to remove any
CO_2 and, if it becomes turbid, add some more HCl and heat again
so that a clear solution is obtained.   Dilute the solution with 150 Cc.

of water, carefully washing off the clock glass with some of the water, and make the solution alkaline with ammonium hydroxide. Precipitate calcium as oxalate with 10 per cent. ammonium oxalate solution, added dropwise, until in excess. Boil the mixture 3 minutes, and let stand three hours. Wash the precipitate, by decantation, with hot water containing some ammonium oxalate, transfer to a filter (preferably ignited asbestos in a Gooch crucible), and complete the washing with cold water. Test the last portion of the washings with a drop of a weak permanganate, which should not be decolorized when acidified with dilute sulphuric acid and a drop of the liquid added. Transfer the washed precipitate, with the filter, to a beaker or remove that adhering to the filter with portions of dilute sulphuric acid, dilute the mixture to 150 Cc. with distilled water and titrate with the $\frac{N}{10}$ permanganate V.S. One drop of the V.S. should be found to produce a distinct pink color, permanent one half minute, on mixing. Carry out a blank titration (in which filter of the same kind and size is used), and apply correction for permanganate consumed in the blank. From the results of two or more titrations calculate the percentage of Ca or CaO in the sample.

The factor for calcium with $\frac{N}{10}$ permanganate is 0.0020045 Gm., for CaO = 0.0028045 Gm., both derived from the equations:

a. $\quad 5CaC_2O_4 + 5H_2SO_4 + 2H_2O = 5CaSO_4 + 5H_2C_2O_4 \cdot 2H_2O.$

b. $\quad \underset{5 \times 126.06}{5H_2C_2O_4 \cdot 2H_2O} + \underset{316.06}{K_2Mn_2O_8} + 3H_2SO_4$

$$= K_2SO_4 + 2MnSO_4 + 10CO_2 + 10H_2O.$$
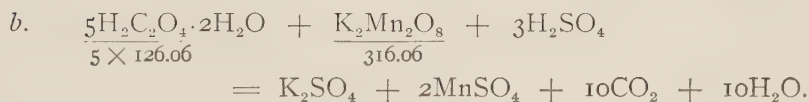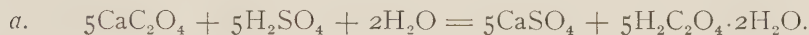
One molecule of permanganate (316.06) reacts with 5 of oxalic acid which were in combination with 5 calcium or 5 CaO. Calcium being 40.09 and CaO = 56.9, 5 × 40.09 of calcium or 5 × 56.09 of calcium oxide corresponds to 316.06 of permanganate.

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 2.0045 Gm. of Ca = 2.8045 Gm. of CaO.

1 Cc. of the V.S. is the equivalent of 0.0020045 Gm. of calcium, and of 0.0028045 Gm. of calcium oxide.

The percentage of Ca or CaO present in the titrated sample is then calculated in usual manner.

Observations.—When a large quantity of impurities is present in the sample, reprecipitation of the calcium oxalate should be carried out. For this purpose the CaC_2O_4 is washed by decantation with ammonium oxalate solution, the precipitate dissolved in minimum dilute HCl, the solution diluted to 100 Cc., made alkaline with ammonium hydroxide, heated to boiling, and the treatment proceeded with as stated above. Since the determination depends on the titration of oxalic acid, which is combined to calcium, the precipitate must be free from soluble oxalates. In connection with washing, it should be remembered that calcium oxalate is appreciably soluble in water and in solutions of other salts than ammonium oxalate.

An alternative method of titration consists of adding to the solu-

tion of the sample a standard oxalic acid V.S. in excess. After boiling, the mixture is made up to definite volume and aliquots of the clear liquid are titrated with the standard permanganate V.S. The volume of standard oxalic acid V.S. consumed by the calcium being thus found, the percentage of the element in the sample is readily calculated. It will be seen that other metals, which form insoluble oxalates, must be absent.

Note.—The above method of titration is applicable to determination of strontium and barium with the only modification that, after precipitation and boiling, the mixture should be allowed to stand, in the case of Sr, during 1 hour, with Ba during 24 hours, before it is filtered.

5. Determination of Lead in the Acetate and Subacetate.

The lead salt is caused to react with an excess of standard oxalic acid and the excess is determined by titration with standard permanganate V.S.

Volumetric solutions employed: $\frac{N}{10}$ oxalic acid and $\frac{N}{10}$ permanganate.

Weigh accurately 0.2 to 0.3 Gm. of the solid or 1 to 1.5 Gm. of a solution of the sample for each titration. Dissolve or dilute with recently boiled distilled water to measure about 20 Cc. Into a 100-Cc. mixing cylinder measure exactly 50 Cc. of $\frac{N}{10}$ oxalic acid V.S., pour in the solution of the sample in a slow stream, mixing well by shaking, and washing the beaker out, into the cylinder, with several small portions of boiled distilled water. Dilute the mixture in the cylinder to a definite volume, shake thoroughly, and let stand to deposit the precipitate. Draw off aliquots of 20 Cc. of the clear liquid for titration. Dilute each with 3 to 4 volumes of water, add 5 Cc. of 10 per cent. sulphuric acid, and titrate with the $\frac{N}{10}$ permanganate V.S.. Of the V.S. one drop should finally impart to the titrated liquid a distinct and permanent pink color. From the volume of $\frac{N}{10}$ oxalic acid consumed by the sample, the quantity and percentage of the lead salt or its equivalent of Pb present are readily calculated. With lead subacetate the reaction is represented by the equations:

$$\underset{548.26}{Pb_2O(C_2H_3O_2)_2} + \underset{2 \times 126.06}{2H_2C_2O_4 \cdot 2H_2O_4}$$

$$= 2PbC_2O_4 + 2C_2H_3O_2 + 3H_2O.$$

$$5H_2C_2O_4 \cdot 2H_2O + \underset{316.06}{K_2Mn_2O_8} + 3H_2SO_4 = etc.,$$
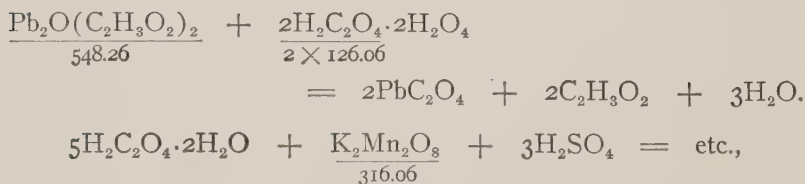
One molecule of oxalic acid (126.06) corresponds to one half of lead subacetate $\left(\dfrac{548.26}{2}\right)$ or to one of lead acetate (379.22).

1 Lt. of $\frac{N}{10}$ oxalic acid contains 6.303 Gm., and corresponds to 13.706 Gm. subacetate.

1 Cc. of the V.S. is, therefore, the equivalent of 0.013706 Gm. of $Pb_2O(C_2H_3O_2)_2$, or of 0.018961 Gm. of $Pb(C_2H_3O_2)_2$, of 0.019961 Gm. $Pb(C_2H_3O_2)_2 \cdot 3H_2O$ and also of 0.010355 Gm. of Pb.

Note.—The formula of the lead subacetate in the above equation is approximate. This method of titration is applicable to the determination of other metals which form insoluble oxalates.

Lead, in lead nitrate or other compounds, may be titrated in alkaline solution with standard permanganate if it be first converted into the nitrate. The V.S. of permanganate should be for this purpose standardized with a standard lead nitrate solution. The titration is carried out by adding an excess of the standard permanganate to a measured volume of the lead nitrate which has been treated with NaOH solution until the precipitate formed just redissolved; the excess of the permanganate is then titrated with some of the standard lead nitrate solution.

$$\underset{6 \times 207.1\,(Pb)}{6Pb(NO_3)_2} \;+\; \underset{316.06}{K_2Mn_2O_8} \;+\; 12NaOH$$
$$= 2MnO_2 + 3Pb_2O_3 + 2KOH + 12NaNO_3 + 5H_2O.$$
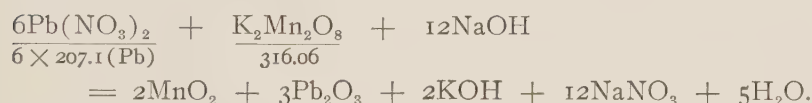
1 Cc. of $\frac{N}{10}$ permanganate V.S. is the equivalent of 0.012426 Gm. of lead.

The presence of bromide, chloride or sulphate, is said not to interfere with the titration; other reactive substances should be absent.

6. Determination of Iron.

A. In Ferrous Compounds.

Volumetric solution employed: $\frac{N}{10}$ potassium permanganate.

Accurately weigh 0.5 of the sample, which should be free from ferric salt, into a titration flask, dissolve in 10 to 15 Cc. of warm 10 per cent. sulphuric acid and titrate with the $\frac{N}{10}$ V.S. Run in the permanganate slowly, mixing well, so that finally one drop of it should produce a distinct pink color, permanent 1 minute. Confirm the accuracy of this by another titration, or several if needed, and, having allowed for the V.S. required for a blank titration, calculate the percentage of iron in the sample. The factor for Fe with $\frac{N}{10}$ permanganate V.S. is 0.005585 Gm., and is derived from the following equation:

$$\underset{10 \times 55.85\,(Fe)}{10FeSO_4} \;+\; \underset{136.06}{K_2Mn_2O_8} \;+\; 8H_2SO_4$$
$$= 5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$
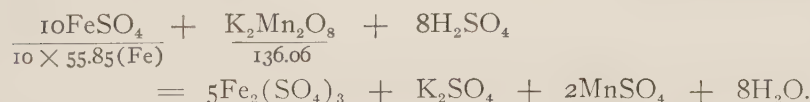
One molecule of permanganate reacts with 10 of ferrous salt containing 10 Fe.

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 5.585 Gm. of iron.

1 Cc. of the V.S. is, therefore, the equivalent of 0.005585 Gm. of Fe.

Observations.—When the object of the titration is to determine

simply the percentage of total iron in a sample, ferrous salts containing ferric salt must be treated as though they were ferric compounds, q. v. To find the amount of Fe present in a sample, as ferrous salt, the titration is carried out as given above. It is evident that other, permanganate reducing substances must not be present in the samples titrated. If chlorides are present the end-reaction will be uncertain and results poor unless manganese sulphate,[1] which is the only effective reagent available, with a little phosphoric acid, is added. The results of titration with permanganate in the presence of chlorides are always high and are supposed to be due to liberation of chlorine and consequent reduction of some of the permanganate. Though manganese sulphate solution does not overcome the action of chlorides entirely, it is very effective when only a small amount of the latter is present.

Fresenius's method of titration, in presence of HCl, is to titrate several portions of the solution, successively, adding each fresh portion to the titrated liquid. The value for the third portion, at which time the HCl is said to have established an equilibrium, is accepted as accurate.

B. In Ferric Compounds.

Weigh accurately from 0.2 to 0.3 Gm. of the sample into a 100-Cc. flask, dissolve in 50 Cc. of 3 per cent. sulphuric acid, add 3 to 5 Gm. of zinc, sensitized with copper (see note, p. 113), close the flask with a stopper provided with a "Bunsen valve" (Fig. 30), and warm on water-bath until all zinc is dissolved and the solution is light green in color. Dilute the solution to 100 Cc. with recently boiled, 10 per cent. sulphuric acid and draw off aliquots for titration with the $\frac{N}{10}$ permanganate V.S. Having made a blank titration in which an equal quantity of the reagents used is treated precisely as in the determination, deduct the volume of the V.S. consumed in the blank and, from the volume of permanganate consumed by the iron, represented by the difference, calculate the percentage of Fe in the sample. The factor with $\frac{N}{10}$ permanganate V.S. for Fe in ferric salts is the same as in ferrous salts as may be seen from the equations:

$$Fe_2(SO_4)_3 + H_2(Zn + H_2SO_4) = 2FeSO_4 + H_2SO_4.$$

$$10FeSO_4 + K_2Mn_2O_8 + 8H_2SO_4 = \text{etc., see under ferrous salts.}$$

1 Cc. of $\frac{N}{10}$ potassium permanganate = 0.005585 Gm. of Fe.

Observations.—Instead of zinc, sheet aluminium may be used. Reduction of ferric compounds before titration is also effected by H_2S, SO_2, $SnCl_2$ or $Ti_2(SO_4)_3$. Other substances which reduce permanganate, and also nitrates and chlorides should be absent. To remove the latter, the iron is precipitated as $Fe(OH)_3$, washed,

[1] Solution of $MnSO_4$: Dissolve 7 Gm. of crystalline $MnSO_4$ in 60 Cc. of water, add 2 Gm. of H_3PO_4 (1.17), 14 Cc. of sulphuric acid (1.82) and dilute to 100 Cc.

dissolved in sulphuric acid and, after reduction, titrated. When chlorides alone are present titration is carried out in the presence of $MnSO_4$ as given under the ferrous salts. Thiocyanate should not be added, as a reagent for Fe, to the solution which is to be titrated.

Note.—To sensitize the zinc, immerse granular zinc in 10 per cent. solution of copper sulphate during 2 to 3 minutes, remove, and dry.

7. DETERMINATION OF MANGANESE DIOXIDE IN PYROLUSITE.

The dioxide reacts with an excess of standard oxalic acid, the unconsumed acid is titrated with permanganate V.S.

Volumetric solutions: $\frac{N}{10}$ permanganate and $\frac{N}{10}$ oxalic acid.

Into a titration flask measure exactly 50 Cc. of $\frac{N}{10}$ oxalic acid V.S., add 5 Cc. of strong sulphuric acid, then 0.15 to 0.25 Gm. of the accurately weighed sample, and heat on water-bath. When the reaction is ended, add 50 Cc. of warm water and titrate with the $\frac{N}{10}$ permanganate V.S. Add the V.S. so that finally, one drop of it should produce a distinct pink color, lasting one half minute. From the volume of $\frac{N}{10}$ oxalic V.S. consumed in this and another check titration, calculate the percentage of MnO_2 in the sample. The factor for MnO_2 with $\frac{N}{10}$ V.S. is 0.004346 Gm., and is derived from the equations:

$$\underset{86.93}{MnO_2} + \underset{126.06}{H_2C_2O_4 \cdot 2H_2O} + H_2SO_4 = MnSO_4 + 2CO_2 + 4H_2O.$$

$$5H_2C_2O_4 + K_2Mn_2O_8 + 3H_2SO_4 = \text{etc.}$$
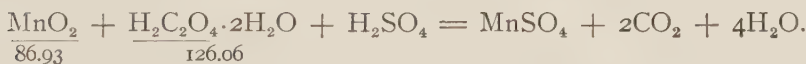
One molecule of MnO_2 (86.93) reacts with one of the acid (126.06) and, since 1 Lt. of $\frac{N}{10}$ oxalic acid contains 6.303 Gm., and corresponds to 4.346 Gm. MnO_2, then

1 Cc. of the V.S. is the equivalent of 0.004346 Gm. of MnO_2.

Notes.—In place of $\frac{N}{10}$ oxalic acid V.S. an excess of a standard solution of ferrous sulphate may be employed. With this reagent, to 0.2 Gm. of the sample placed in a small flask provided with a " Bunsen valve," are added 50 Cc. of the recently standardized $FeSO_4$ solution (see 11, p. 117), and the closed flask is heated on water-bath until the MnO_2 is decomposed, usually indicated by the color of the residue which should not be dark under these conditions. After cooling and diluting with boiled, diluted sulphuric acid, the unconsumed $FeSO_4$ is titrated with the standard permanganate V.S. From the quantity of ferrous sulphate oxidized by the dioxide ($MnO_2 + 2FeSO_4$), the percentage of MnO_2 in the sample is calculated.

Small quantities of Mn (in water) are determined by the method of Knorre. Of water, 5 Lt. are evaporated to dryness with dilute sulphuric acid, the residue heated with $KHSO_4$, dissolved in water and the solution filtered. The filtrate diluted to 150 Cc. is acidified with 5 Cc. of $1 + 3$ sulphuric acid, and boiled with 20 Cc. of

9

6 per cent. ammonium persulphate to precipitate Mn as MnO_2. After cooling, 10 Cc. of 0.17 per cent. H_2O_2 are added, and the unconsumed hydrogen dioxide titrated with $\frac{N}{10}$ permanganate V.S. From the volume of the hydrogen dioxide, the strength of which is found by titration with $\frac{N}{10}$ permanganate V.S. at the time of the determination, the quantity of Mn present is calculated. Solid samples are dissolved and treated in like manner. For colorimetric determination of Mn see Chapter V.

8. Determination of Copper.

Cuprous oxide is dissolved in an excess of ferric salt solution and titrated with standard permanganate.

Volumetric solution required: $\frac{N}{10}$ permanganate.

A suitable quantity of the sample (0.1 Gm.) of copper salt, is dissolved in water, 1 per cent. solution of sodium carbonate is added in excess, the mixture heated to boiling, and the copper precipitated as Cu_2O with a slight excess of 10 per cent. solution of glucose, added until the blue color disappears. After boiling 10 minutes the precipitate is filtered off through asbestos in a Gooch crucible, washed with hot water and then transferred, with the crucible, to a spacious flask previously filled with CO_2. Solution of pure ferric sulphate is then added, together with strong sulphuric acid, and, when the Cu_2O has dissolved, the solution is titrated with the $\frac{N}{10}$ permanganate V.S.

1 Cc. of $\frac{N}{10}$ permanganate V.S. corresponds to 0.00636 Gm. of Cu. For exact results the permanganate V.S. should be standardized with pure (electrolytic) copper, the method of determination being closely adhered to in the standardization.

Note.—The Cu_2O obtained in the determination of sugars or other Cu reducing substances may be titrated directly with the standard permanganate V.S. The precipitate, weighing not more than 0.2 Gm., is filtered through asbestos in a Gooch crucible or on a porcelain plate and after washing with water is returned to the beaker from which it came, covered with 80 to 100 Cc. of diluted sulphuric acid, 25 Cc. of $\frac{N}{10}$ permanganate are added and the mixture is stirred until the red oxide has completely dissolved. Boiling water is added to bring the temperature of the solution to 40° or 50° C., an excess of $\frac{N}{10}$ oxalic acid introduced and the excess titrated with the $\frac{N}{10}$ permanganate V.S. From the volume of standard permanganate consumed by the Cu_2O the percentage of Cu, or of the particular reducing agent which produced it, may be calculated.
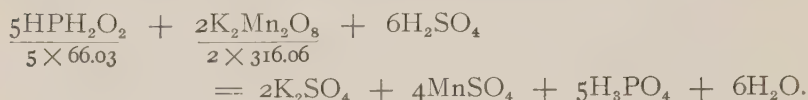
9. Determination of Nitrites.

Nitrites are oxidized to nitrates by an excess of standard permanganate, the excess of which is titrated with standard oxalic acid.

Volumetric solutions employed: $\frac{N}{10}$ permanganate and $\frac{N}{10}$ oxalic acid.

Prepare a solution of the sample of a definite strength (1–100). Into a titration flask, measure accurately 40 to 50 Cc. of $\frac{N}{10}$ permanganate V.S., add 20 to 30 Cc. of 10 per cent. sulphuric acid

and then enough of the sample solution to contain from 0.1 to 0.15 Gm. of the salt. Dilute the solution to 300 or 400 Cc., heat at 40° C. during 10 minutes, and titrate with the $\frac{N}{10}$ oxalic acid V.S. Add the V.S. in small portions, reducing these to drops towards the end, so that finally one drop should discharge the pink color of the permanganate. From the volume of $\frac{N}{10}$ permanganate V.S. consumed by the sample, represented by the difference of the solutions used, calculate the percentage of the particular nitrite determined. The factor for any nitrite is derived from an equation representing the reaction of it with permanganate. Thus, for sodium nitrite, the factor is 0.0034505 Gm., and is obtained from the equation:

$$\frac{5NaNO_2}{5 \times 69.01} + \frac{K_2Mn_2O_8}{316.06} + 3H_2SO_4$$
$$= K_2SO_4 + 2MnSO_4 + 5NaNO_3 + 3H_2O.$$
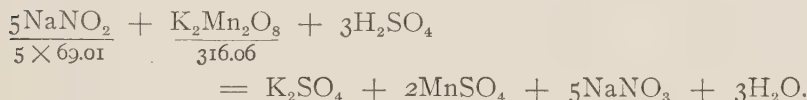
This shows that $5NaNO_2$ (5×69.01) react with $K_2Mn_2O_8$ (316.06) and, since 1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 5×0.6901 Gm. $NaNO_2$, then

1 Cc. of the V.S. is the equivalent of 0.0034505 Gm. of sodium nitrite.

In like manner, the factor for any other nitrite is found, or if desired, the NO_2 or nitrogen equivalent of any nitrite may be derived, and the factor used in calculation of results to be expressed as percentage of NO_2 or nitrogen.

Observations.—Nitrous acid being volatile, the order of addition of reagents given in the method must be observed. The titration of the excess of $\frac{N}{10}$ permanganate by $\frac{N}{10}$ oxalic acid V.S. is not always satisfactory; as an alternative, the acid may be added in excess and the excess then titrated with the permanganate, in which case the volumes of permanganate V.S. used are added and, from the sum, the volume of the oxalic V.S. acid is deducted.

A direct titration of a definite volume of the $\frac{N}{10}$ permanganate V.S., mixed with dilute sulphuric acid with a solution of the nitrite of known strength, may also be made. The solution of the sample is run in slowly from a burette, in gradually decreasing portions, so that one drop of the liquid should finally discharge the pink color of the permanganate. Calculations of percentage of the nitrite are based on the quantity of the sample required to decolorize a given volume of the standard permanganate V.S.

10. DETERMINATION OF NITRATES.

(Method of Pelouze and Fresenius.)

The nitrate, reacting with an excess of ferrous chloride, oxidizes an equivalent quantity of it; the unchanged chloride is then titrated with permanganate.

Volumetric solutions required: $\frac{N}{10}$ permanganate and a standard ferrous chloride. The latter is prepared by dissolving about 1 Gm. (accurately weighed) of clean iron wire, of known Fe content, in

20 to 25 Cc. of strong HCl, specially free from HNO_3, in a flask in which air has been replaced by CO_2. While the iron is being dissolved on steam-bath, and during the subsequent cooling of the solution, a current of CO_2 should be kept continually passing through the flask.

Prepare a solution of the sample, 10 Cc. to contain 0.1 to 0.2 Gm. of the nitrate. By means of a pipette introduce exactly 10 Cc. of the solution into the flask containing the $FeCl_2$ solution by opening the stopper slightly or inserting the pipette into the opening in the stopper, occupied by a glass tube, heat on water-bath until the reaction subsides and then boil gently during 10 to 15 minutes. Cool and dilute the solution to a definite volume with recently boiled, distilled water and titrate aliquots with the $\frac{N}{10}$ permanganate, adding to each portion of the titrated solution 10 Cc. of manganese sulphate solution (see p. 112). From the quantity of iron oxidized by the nitrate, calculate percentage of the nitrate, or its radicle NO_3, or the equivalent of nitrogen then present in the sample. To find the needed factor the reactions are represented by equations as, for example, in the case of potassium nitrate:

$$\underset{2 \times 101.11}{2KNO_3} + \underset{6 \times 55.85\,(Fe)}{6FeCl_2} + 8HCl = 6FeCl_3 + 2KCl + 2NO + 4H_2O.$$

$$10FeCl_2 + \underset{316.3}{K_2Mn_2O_8} + 16HCl$$
$$= 10FeCl_3 + 2KCl + 2MnCl_2 + 8H_2O.$$
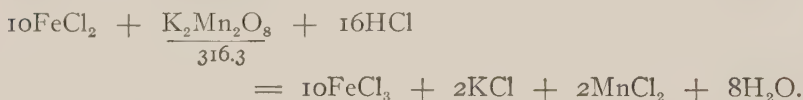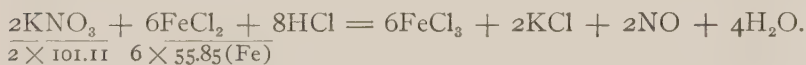
One molecule of KNO_3 (101.11) oxidizes 3 molecules of $FeCl_2$ (3×55.85 Fe) to ferric salt. But one permanganate oxidizes 10 molecules of $FeCl_2$ or 10 Fe (55.85) as ferrous salt, therefore, 55.85 Gm. correspond to $\frac{101.11}{3}$, or 33.7 Gm. KNO_3 or 20.7 Gm. of NO_3. By proportion:

$$55.85 : 33.7 :: 1 : x.$$
$$x = 0.6034.$$

One (1) Gm. of Fe corresponds to 0.6034 Gm. of KNO_3 or 0.37 Gm. NO_3.

1 Cc. of $\frac{N}{10}$ permanganate V.S. is the equivalent of 0.005585 Gm. of Fe.

The exact quantity of iron in the solution being known, and the quantity of it oxidized by the permanganate being found by titration, the difference of these constitutes the iron oxidized by the sample. From these results the percentage of a nitrate or NO_3 is then calculated.

Illustration.—Of iron wire, 99.7 per cent. pure, 0.875 Gm. were dissolved in HCl, a sufficient volume of a solution of sodium nitrate to contain 0.1 Gm. of the sample added, the solution after oxidation made up to 100 Cc. and titrated in 25 Cc. portions. These required

30.1, 30.8 and 30.6 Cc. of $\frac{N}{10}$ permanganate V.S. respectively; to find the percentage of $NaNO_3$ in the sample.

Since three fourths (75 Cc.) of the unoxidized $FeCl_2$ consumed 91.5 Cc. (30.1 + 30.8 + 30.6) of $\frac{N}{10}$ permanganate V.S. then, to oxidize the excess of $FeCl_2$, would require 122 Cc. of the permanganate. But, one Cc. of $\frac{N}{10}$ permanganate V.S. corresponds to 0.005585 Gm. of iron. Now, the quantity of Fe dissolved (0.875 Gm. of 99.7 per cent.) = 0.87255 Gm.; the quantity of Fe unoxidized is found by titration = 0.68137 Gm.; the quantity of Fe oxidized by sample = 0.19118 Gm.

Since 1 Gm. of Fe corresponds to 0.50743 Gm. of $NaNO_3$ as found by proportion:

$$55.85 : 28.34 :: 1 : x.$$

then:

$$\frac{0.19118 \times 0.50743 \times 100}{0.1} = 97.01.$$

The sample is therefore found to contain 97.01 per cent. of $NaNO_3$.

Observations.—It is important that, beside the nitrate, no other oxidizing agent acting on the $FeCl_2$ be present and that the reaction of the nitrate with the ferrous salt be completed. To prevent entrance of air during treatment, the tube through which the CO_2 escapes should be made long enough, and bent at 45°, to reach into a beaker containing water. Sulphate of iron can not be satisfactorily used in place of the $FeCl_2$.

Note.—Instead of titrating the excess of $FeCl_2$, the ferric chloride produced in the reaction may be determined iodometrically (see determination of ferric salts by titration with thiosulphate).

11. Determination of Chlorates.

The chlorate is caused to react with ferrous salt in excess and the unoxidized salt titrated with permanganate.

Volumetric solutions required: $\frac{N}{10}$ permanganate and standard ferrous sulphate. The ferrous sulphate solution is prepared by dissolving 28 to 30 Gm. of crystalline ferrous sulphate in water to measure 950 Cc. and adding to the solution 50 Cc. of concentrated sulphuric acid. The exact strength of the solution, which will then be nearly $\frac{N}{10}$, is found by titration at the time of the determination.

Dissolve about 0.5 Gm. of the sample of chlorate, weighing accurately, in water, to measure exactly 100 Cc. Transfer 10 Cc. of the solution to a 200-Cc. flask provided with a Bunsen valve, see p. 97, pass CO_2 through the flask to remove all air, close the flask and boil contents gently during 10 to 15 min. Cool the solution, dilute it with an equal volume of cold, recently boiled distilled water and titrate with the $\frac{N}{10}$ permanganate, using 10 Cc. of manganese sulphate solution (p. 112). From the quantity of iron in the ferrous sulphate oxidized by the chlorate, calculate the per-

centage of the particular chlorate present in the sample.   The reactions are represented:

$$\underset{122.56}{KClO_3} + \underset{6 \times 55.85(Fe)}{6FeSO_4} + 3H_2SO_4 = KCl + 3Fe_2(SO_4)_3 + 3H_2O.$$

$$\underset{10 \times 55.85(Fe)}{10FeSO_4} + \underset{316.06}{K_2Mn_2O_8} + 8H_2SO_4$$

$$= 10Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O.$$
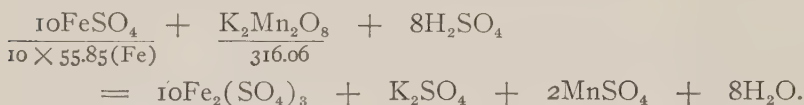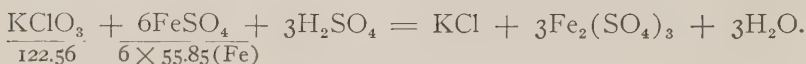
The oxygen of one molecule of chlorate (122.56) oxidizes 6 atoms of iron as ferrous salt (6 × 55.85), while one permanganate oxidizes 10 atoms of Fe; so that:

$$KClO_3 = 6FeSO_4 = \frac{6}{10}\,K_2Mn_2O_8, \text{ or } K_2Mn_2O_8 = \frac{10}{6}\,KClO_3.$$
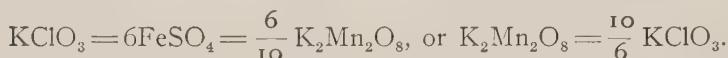
1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 2.0425 Gm. of $KClO_3$.

1 Cc. of the V.S. is, therefore, the equivalent of 0.0020425 Gm. of potassium chlorate.

Illustration.—Quantity of sample of $KClO_3$ employed in titration =0.048 Gm.; $\frac{N}{10}$ permanganate required for 50 Cc. of $FeSO_4$ solution = 52.4 Cc.; $\frac{N}{10}$ permanganate required for excess of $FeSO_4$ in determination, 29.2 Cc.; $\frac{N}{10}$ permanganate, which corresponds to chlorate present, 23.2 Cc.; to calculate the percentage of $KClO_3$ in the sample.   By rule on p. 24,

$$\frac{0.0020425 \times 23.2 \times 100}{0.048} = 98.72.$$

The sample is found to contain 98.72 per cent. of $KClO_3$.

12. DETERMINATION OF PERSULPHATES.

Persulphates, not decolorizing permanganate readily, are caused to react with ferrous sulphate in excess and the excess of the salt is then titrated with permanganate.

Volumetric solutions employed: $\frac{N}{10}$ permanganate and standard ferrous sulphate (see 11).

Displace the air in a small flask with CO_2, introduce 30 Cc. of recently standardized $FeSO_4$ or $(NH_4)_2Fe(SO_4)_2$ of about $\frac{N}{10}$ strength, drop in 0.2 to 0.3 Gm. of the accurately weighed sample and close the flask with a stopper provided with a "Bunsen valve." Shake the mixture well while warming on water bath.   When the reaction is completed, cool, dilute with 70 Cc. of recently boiled distilled water and titrate with $\frac{N}{10}$ permanganate V.S.   From the quantity of the ferrous salt oxidized by the persulphate, calculate the percentage of the persulphate in the sample.   Reactions:

$$\underset{270.34}{K_2S_2O_8} + \underset{2 \times 151.92}{2FeSO_4} = Fe_2(SO_4)_3 + K_2SO_4.$$

$$10FeSO_4 + \underset{316.06}{K_2Mn_2O_8} + 8H_2SO_4 = \text{etc.}$$
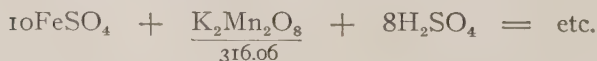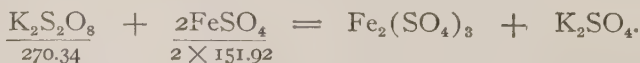
316.06 Gm. of permanganate correspond to 5×270.34 or 1351.7 Gm. of potassium persulphate.

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 13.517 Gm. $K_2S_2O_8$.

1 Cc. of the V.S. is the equivalent of 0.013517 Gm. of potassium persulphate.

Note.—Heating of the solution at 60° C. during 10 minutes and cooling in CO_2 during 12 hours, then titrating with standard permanganate V.S. has been recommended.

13. Determination of Percarbonates and Perborates.

These compounds react with dilute acids, giving hydrogen dioxide, which is titrated.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

From 0.2 to 0.3 Gm. of the sample, accurately weighed, are dropped into 300 Cc. of cold diluted (10 per cent.) sulphuric acid and, when completely dissolved, the liquid is titrated with $\frac{N}{10}$ permanganate V.S. The reaction is completed when one drop of the V.S. is found to have imparted to the liquid a distinct pink color, permanent one half minute on mixing. Calculation of the percentage of the particular percarbonate or perborate present in the sample is made with factors derived from equations representing the reactions involved. Thus, for instance:

1.　$\underset{216.22}{\underline{K_2C_2O_6 \cdot H_2O}} + 2H_2SO_4 = 2KHSO_4 + 2CO_2 + H_2O_2 + H_2O.$

2.　$\underset{154.1}{\underline{NaBO_3 \cdot 4H_2O}} \quad + \quad H_2SO_4$

$$= NaHSO_4 + B(OH)_3 + H_2O_2 + 2H_2O.$$

$$5H_2O_2 + \underset{316.06}{\underline{K_2Mn_2O_8}} + 3H_2SO_4$$

$$= K_2SO_4 + 2MnSO_4 + 10O + H_2O.$$
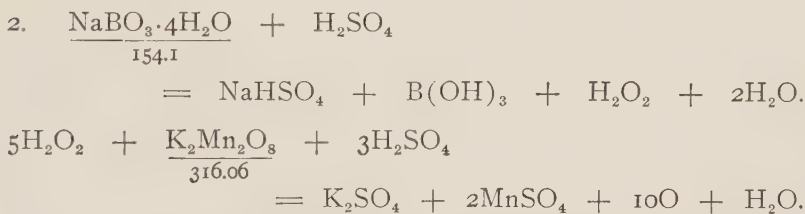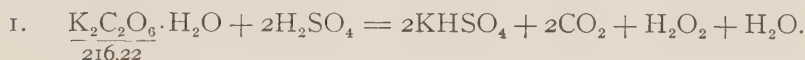
1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 1.701 Gm. H_2O_2.

1 Cc. of the V.S. is, therefore, the equivalent of 0.007705 Gm. perborate, and of 0.010811 Gm. percarbonate.

14. Determination of Hypophosphorous Acid.

The acid is oxidized with an excess of standard permanganate, and the excess of this is titrated with standard oxalic acid.

Volumetric solutions employed: $\frac{N}{10}$ permanganate and $\frac{N}{10}$ oxalic acid.

Weigh accurately 3 to 5 Gm. of the sample, dilute with water to measure exactly 100 Cc. Into a titration flask introduce 50 Cc. of $\frac{N}{10}$ permanganate V.S., add 10 Cc. of 10 per cent. sulphuric acid, then 10 Cc. of the solution of the sample, and heat to boiling. After

15 minutes boiling, cool somewhat and titrate, while warm, with the $\frac{N}{10}$ oxalic acid V.S. The oxalic acid should be run into the colored liquid, in small portions, with agitation, until the final pink color of the solution is discharged by one drop of the oxalic acid V.S. From the volume of $\frac{N}{10}$ permanganate consumed by the sample, calculate the percentage of the acid present. The factor for hypophosphorous acid with $\frac{N}{10}$ permanganate is 0.00165075 Gm., and is derived from the following equation:

$$\underset{5 \times 66.03}{5HPH_2O_2} + \underset{2 \times 316.06}{2K_2Mn_2O_8} + 6H_2SO_4$$
$$= 2K_2SO_4 + 4MnSO_4 + 5H_3PO_4 + 6H_2O.$$

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 1.65075 Gm. HPH_2O_2.

1 Cc. of the V.S. is, therefore, the equivalent of 0.00165075 Gm. of hypophosphorous acid.

Observation.—Other reducing agents than hypophosphorous acid must not be present. Hypophosphites, yielding hypophosphorous acid with sulphuric acid, may be determined by the same method. For one titration only about 0.1 Gm. of the salt should be taken, while the volume of H_2SO_4 added is increased. If the end-reaction is obtained with difficulty, an excess of the oxalic acid may be added and titration completed with $\frac{N}{10}$ permanganate V.S.

15. DETERMINATION OF PERMANGANATES.

Volumetric solution employed: $\frac{N}{10}$ oxalic acid.

Titration of permanganate with $\frac{N}{10}$ oxalic acid is carried out after the method given for the standardization of potassium permanganate V.S., p. 96, the solution of the sample of definite strength being used for titration of a definite volume of the $\frac{N}{10}$ oxalic acid V.S. Since 1 Cc. of $\frac{N}{10}$ oxalic acid V.S. corresponds to 0.0031606 Gm. of potassium permanganate, the quantity of permanganate in the volume of the solution of sample is readily calculated.

Note.—Permanganate may also be determined by titration with $\frac{N}{10}$ arsenous acid V.S. used in excess. The mixture is heated until the supernatant liquid is clear, then filtered, washed, and in the filtrate, neutralized with HCl, the unconsumed As_2O_3 titrated with $\frac{N}{10}$ iodine V.S. in the presence of sodium bicarbonate. (See iodometric titrations.)

Residual titration with $\frac{N}{10}$ oxalic acid and $\frac{N}{10}$ permanganate is also made use of in this determination (U.S.P. method).

16. DETERMINATION OF FERROCYANIDE.   (De Hean.)

Volumetric solution employed: $\frac{N}{10}$ permanganate.

Dissolve about 1 Gm. of the sample, accurately weighed, in 100 Cc. of water, acidify the solution with 10 per cent. sulphuric acid and titrate with the standard V.S. Add the permanganate to the milky mixture, in small portions, reducing the flow to drops as

soon as a change from yellow color to greenish is observed. When a distinct pink color appears the end-point is reached. For calculation of the percentage, the factor for potassium ferrocyanide, which is 0.036856 Gm. with $\frac{N}{10}$ V.S., is derived from the equation:

$$\frac{10K_4FeCN_6 \cdot 3H_2O}{10 \times 422.37} + \frac{K_2Mn_2O_8}{316.06} + 8H_2SO_4$$

$$= 10K_3FeCN_6 + 6K_2SO_4 + 2MnSO_4 + 11H_2O.$$
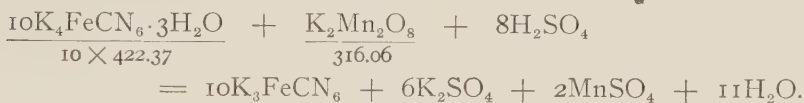
1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 42.237 Gm. of $K_4FeCN_6 \cdot 3H_2O$.

1 Cc. of the V.S. is, therefore, the equivalent of 0.042237 Gm. of potassium ferrocyanide.

17. DETERMINATION OF FERRICYANIDE.

Ferricyanide is reduced to ferrocyanide in alkaline solution by $FeSO_4$ and the ferrocyanide is then titrated with permanganate.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

Dissolve a suitable quantity of the sample (0.5 Gm.) in water, make alkaline with KOH, adding enough of the solution to introduce 0.4 Gm. of the hydroxide, heat to boiling, and add an excess of ferrous sulphate solution or about 0.2 Gm. of the crystalline salt for each 0.1 Gm. of the sample used. Heat the mixture until a black precipitate of ferro-ferric hydroxide separates, then cool, dilute with water to make the mixture measure 250 Cc., and titrate the clear supernatant liquid in aliquots of 50 Cc. Before the addition of the V.S. acidify with sulphuric acid and then titrate the ferrocyanide, adding the V.S. in small portions until a pink color is imparted to the titrated liquid. From the permanganate consumed the percentage of the ferricyanide present is calculated. The reactions are represented:

$$\frac{K_3FeCN_6}{329.21} + 2Fe(OH)_2 + KOH = K_4FeCN_6 + Fe_2(OH)_5.$$

$$10K_4FeCN_6 + \frac{K_2Mn_2O_8}{316.06} + 3H_2SO_4 = \text{etc., see above}$$
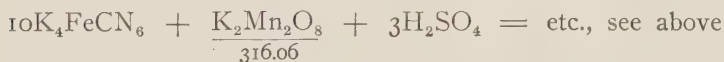
Since ferricyanide gives ferrocyanide, and ten molecules of the latter require one of permanganate for oxidation, it will be seen that 1 Cc. of $\frac{N}{10}$ permanganate, which contains 0.0031606 Gm., is the equivalent of 0.032921 Gm. of potassium ferricyanide.

Observations.—It is important to adjust the quantities of KOH and of $FeSO_4$ in this determination. While an excess of ferrous sulphate in relation to the ferricyanide is necessary, the KOH must be present in sufficient quantity to supply the needed potassium as well as to precipitate all the iron in the sulphate as hydroxide.

18. DETERMINATION OF HYDROGEN SULPHIDE.   (Mohr.)

Hydrogen sulphide reduces ferric salts to ferrous, the reduced salt is titrated with permanganate.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

A suitable volume of ferric sulphate solution, free from ferrous salt, in diluted sulphuric acid is carefully measured into a small flask from which the air has been removed by CO_2, 10–25 Cc. of the solution of H_2S are then run in from a pipette, the flask securely closed and, after mixing, allowed to stand 1 hour. For titration the liquid is diluted with recently boiled distilled water and titrated with the $\frac{N}{10}$ permanganate V.S. in the usual manner. The separated sulphur has no effect on the results. The pink color of permanganate should last at least one half minute. For calculation of the percentage the factor for H_2S with $\frac{N}{10}$ V.S., which is 0.001604 Gm., is derived from the equations:

$$Fe_2(SO_4)_3 \; + \; \underset{34.09}{H_2S} \; = \; 2FeSO_4 \; + \; H_2SO_4 \; + \; S.$$

$$10FeSO_4 \; + \; \underset{316.06}{K_2Mn_2O_8} \; + \; 8H_2SO_4$$
$$= \; 10Fe_2(SO_4)_3 \; + \; K_2SO_4 \; + \; 2MnSO_4 \; + \; 8H_2O.$$
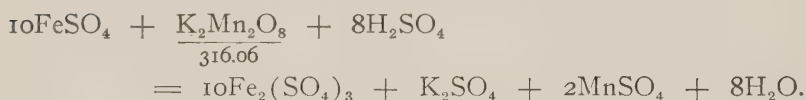
One H_2S reduces 2 Fe from ferric to ferrous, or one Fe corresponds to $\frac{H_2S}{2}$. One molecule of permanganate (316.06) therefore corresponds to 5×34.09 or 170.45 parts of H_2S.

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606 Gm., and corresponds to 1.7045 Gm. of H_2S.

1 Cc. is, therefore, the equivalent of 0.0017045 Gm. of hydrogen sulphide.

The above method is applicable to determination of other sulphides and also of such metals as cadmium and zinc. The sulphides of these metals are precipitated, washed, treated with sulphuric acid in presence of the ferric sulphate, in a closed bottle, and the ferrous salt produced titrated as above. From the quantity of the ferrous salt produced, or rather the volume of permanganate consumed, the percentage of the particular metal is calculated.

The time required for decomposition may be shortened to one half if the mixture be heated in a pressure vial on water-bath.

19. DETERMINATION OF FORMIC ACID.

Volumetric solution employed: $\frac{N}{10}$ permanganate.

Weigh accurately about one (1) Gm. of the sample into a 250-Cc. measuring flask, dilute to the mark with water, at standard temperature, and employ 20 Cc. portions for titration. Neutralize the acid to be titrated with a slight excess of sodium carbonate, heat to 80° C. and titrate with $\frac{N}{10}$ permanganate V.S. Add the V.S. in such a manner that one drop will finally impart a distinct pink color to the titrated liquid. From the average volume of several titrations, calculate the percentage of the acid in sample. The reaction is represented by the equation:

$$\underset{3 \times 46.02}{3HCOOH} + \underset{316.06}{K_2Mn_2O_8} = K_2CO_3 + 2CO_2 + 2MnO_2 + 3H_2O.$$

316.06 parts of permanganate oxidize 3×46.02 parts of formic acid.

1 Lt. of $\frac{N}{10}$ permanganate contains 3.1606, and corresponds to (0.4602×3) 1.3806 Gm. HCOOH.

1 Cc. of the V.S. is, therefore, the equivalent of 0.0013806 Gm. of formic acid.

Observations.—Formic acid is not readily oxidized in cold solutions, requiring 6 or more hours at room temperature. For titration the acid must be neutralized to prevent loss by volatilization.

This method of titration may be also employed for the determination of formaldehyde. The oxidation in that case requires only one hour in the cold and is best made with an excess of the permanganate V.S., a measured volume of which is added. The excess of the permanganate may then be found by titration with $\frac{N}{10}$ oxalic V.S., titrating at 40° C., or by adding an excess of this V.S. and titrating with $\frac{N}{10}$ permanganate V.S.

The permanganate method not being entirely reliable, the hypobromite method, see p. 154, has been advanced to supersede it.

20. DETERMINATION OF TANNIN.

(Loewenthal's Method, Proctor's Modification.)

Tannin is oxidized by standard permanganate, the titration being carried out in the presence of indigo solution.

Volumetric solution required: $\frac{N}{25}$ potassium permanganate, accurately standardized with $\frac{N}{10}$ oxalic acid V.S.

Indicator: Indigo solution. 6 Gm. indigo carmine, H_2SO_4 50 Cc. + H_2O to make 1000 Cc.

Dissolve 2–3 Gm. of a sample of tannic acid in water and dilute the solution or an infusion of 5 Gm. of the drug, prepared with 400 Cc. of water, to measure, in the cold, 500 Cc. For titrations employ 10 Cc. of the diluted solution.

To 25 Cc. of indigo solution, accurately measured, add 10 Cc. of the solution of sample, then 700 Cc. of water and titrate with the standard permanganate V.S. Add the V.S. in small portions, stirring well, until the titrated liquid becomes light green, then reduce the flow to drop at a time so that finally one drop of the V.S. produces a bright yellow to pinkish color. The volume of $\frac{N}{25}$ permanganate V.S. consumed designate as (*a*).

To determine and allow for the effect on permanganate of substances other than tannin, the tannin is precipitated and removed. Hide powder or gelatin is used.

To exactly 100 Cc. of the sample solution add 50 Cc. of a gelatin solution, 2.5 per cent. in saturated sodium chloride, then 100 Cc. of a solution of 97.5 Cc. of saturated NaCl and 2.5 concentrated H_2SO_4, add some kaolin or granulated talc and mix well by shaking several minutes. Let settle, filter the clear solution, rejecting first portion,

then take 25 Cc. of the filtrate (corresponding to 10 Cc. sample solution), together with 25 Cc. of the indigo solution, both accurately measured, and dilute with 700 Cc. of H_2O as given above. The $\frac{N}{25}$ permanganate V.S. should be run in cautiously to the production of yellow to pinkish color, matching that of the first titration. The volume of the V.S. consumed is represented by (b); $a - b = c$, which represents the volume of permanganate consumed in the oxidation of tannin. The calculation is then made through $\frac{N}{10}$ oxalic acid V.S., 1000 Cc. of which are assumed to correspond to 4.157 Gm. of tannin (gallotannic acid).

For pure tannin solutions the second titration may be replaced by a blank titration in which 25 Cc. of the indigo solution, diluted with 700 Cc. water, are titrated with the standard permanganate, $a - b = c$, as above. The success of these titrations depends on identity of conditions, and careful measuring.

The value of standard permanganate or of oxalic acid through the permanganate is established by titration of a pure tannic acid solution of definite strength. The standard solution is made about 0.3 per cent., the purest obtainable tannin (not less than 95 per cent. by hide powder) being employed.

Solutions of samples for titration should be made at 50° C., crude drugs or powders being extracted by infusion and percolation until the sample is exhausted. (Test last portion with ferric chloride.) Extracts or strong solutions are diluted to contain 0.6 to 0.8 Gm. of solid matter in 100 Cc.

In wine, tannin and color are jointly determined. The alcohol in 100 Cc. of wine is removed by evaporation and the loss of liquid made up by addition of water. 5 to 10 Cc. of the alcohol-free wine are mixed with 25 Cc. of indigo solution, diluted with 1000 Cc. of water, and titrated with $\frac{N}{25}$ permanganate V.S. to the production of yellow color. Volume consumed $= (a)$.

An equal volume of the alcohol-free solution of sample is mixed with purified animal charcoal, shaken during 15 minutes, filtered, and the charcoal washed thoroughly with water. The filtrate and washings are diluted to measure 1000 Cc., and the liquid is titrated with $\frac{N}{25}$ permanganate V.S. The number of Cc. of the V.S. consumed $= (b)$; $a - b = c$, representing in Cc. the volume of $\frac{N}{25}$ permanganate consumed in oxidation of tannin and coloring matter in 10 Cc. of wine. To calculate, the equivalents above given are used.

In spices, tannin is determined by titration of an infusion of the sample prepared after 24 hours extraction, with ether, in a soxhlet extractor. 2 Gm. are so treated and the residue is boiled with 300 Cc. of water during 2 hours, diluted to 500 Cc. and filtered. Aliquots of 25 Cc. are titrated with permanganate V.S. and indigo as given above.

21. DETERMINATION OF NITRATES. (Vriens.)[1]

Nitrate, in solution containing sulphuric acid, oxidizes ferrous to ferric salt; add K_3FeCN_6 and the color produced will depend on the " ic " or " ous " salt present.

[1] Ztsch. anal. Chem., 1907, 46, p. 414.

Volumetric solution required: Standard ferrous ammonium sulphate (Mohr's salt). Prepared by dissolving 25 Gm. of the crystalline salt, in water, to measure 1000 Cc., and adding a little sulphuric acid. The exact strength of the V.S. is established by titration with $NaNO_3$ solution, 5 Gm. to 1 Lt.

Indicator: Potassium ferricyanide solution 0.1 per cent.

The sample of nitrate (about 5 Gm.) to be determined is carefully weighed, dissolved to measure exactly 1000 Cc., and, if need be, the solution filtered. Of the clear solution, 10 Cc. are accurately measured into a 200-Cc. erlenmeyer, 10 Cc. of concentrated H_2SO_4 added, then, from a burette, the standard $(NH_4)_2Fe(SO_4)_2$ V.S. run in and 1 Cc. of the indicator introduced. The color produced should be observed within one half minute, a greenish color appearing on longer standing. If the color produced is blue, less of the V.S. must be added next time. The titration is repeated with fresh 10 Cc. portions until the color of the end-reaction is just brown or brownish-green, when a volume of the V.S., 0.1 Cc. greater, gives a blue color. From the volume of standard ammonium ferrous sulphate V.S. required to react with the nitrate present, the percentage of the latter in sample is calculated, the factor having been found by standardization of the V.S. with pure nitrate.

Oxidizable substances which react with the nitrate as well as oxidizing agents acting like the nitrate must not be present.

B. Titrations with Standard Potassium Dichromate V.S.

22. Determination of Ferrous Salts.

Ferrous salts are oxidized to ferric; the end-reaction is indicated when a drop of the titrated liquid no longer reacts with the ferricyanide.

Volumetric solution employed: $\frac{N}{10}$ dichromate.

Indicator: Solution of potassium ferricyanide, 2 per cent. (must be free from ferrocyanide).

Accurately weigh from 2 to 3 Gm. of the sample, dissolve in water, to measure exactly 100 Cc.; of saccharated ferrous carbonate 1.5 to 2 Gm. are dissolved in 15 Cc. dilute sulphuric acid and the solution diluted to 100 Cc. Measure into a beaker 10 Cc. of the solution, dilute with water to 100, then add 5 Cc. of 10 per cent. sulphuric or hydrochloric acid and titrate with the $\frac{N}{10}$ dichromate V.S. For a trial titration, run the V.S. into the titrated liquid in 1 Cc. portions, mixing after each addition, and testing the titrated liquid, after each addition, when nearly all of the ferrous salt has been oxidized. For this purpose, mix the liquid well, remove a drop of it to a clean, white porcelain plate, and bring in contact with it a drop of the indicator. When an instantaneous bluish color is no longer produced, read the burette and use the result as a guide for the subsequent titrations which are to be more carefully performed. In these titrations, run in of the dichromate V.S. as much as will oxidize nearly all the ferrous salt, and complete the titration by adding the V.S. in 2 to 3 drop portions at a time and testing for the end-point

after each addition in the manner given. When finally 2 drops of the V.S. are added and the titrated liquid, after mixing, gives no blue color with a drop of the indicator, the reaction is completed, and the reading of the burette taken just before the last portion has been added, is accepted. From the volume of the V.S. required for oxidation and found as the result of several titrations the percentage of the Fe in sample is calculated.

The factor for Fe as ferrous salt with $\frac{N}{10}$ dichromate V.S. is 0.005585 Gm. and is derived from the following equation:

$$
\begin{array}{l}
\underset{\substack{6 \times 151.92 \\ 6 \times 55.85\,(Fe)}}{6FeSO_4} \;+\; \underset{294.4}{K_2Cr_2O_7} \;+\; 8H_2SO_4 \\[2mm]
\qquad = Cr_2(SO_4)_3 \;+\; 3Fe_2(SO_4)_3 \;+\; 7H_2O \;+\; 2KHSO_4.
\end{array}
$$
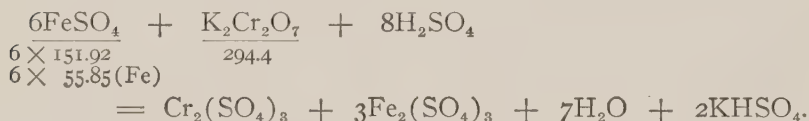
One molecule of potassium dichromate (294.4) reacts with six (6) of ferrous sulphate, $6 \times 151.92 = 6 \times 55.85$ Fe. One Fe then corresponds to one sixth of dichromate.

1 Lt. of $\frac{N}{10}$ dichromate contains 4.9066 + Gm., and corresponds to 5.585 Gm. Fe.

1 Cc. therefore is the equivalent of 0.005585 Gm. of Fe.

To calculate percentage:

$$
\frac{\text{Vol. of } \frac{N}{10} \text{ dichromate} \times 0.005585 \times 100}{\text{Weight of sample}} = \text{per cent. of Fe.}
$$

Observation.—While the end-point is not very sharply indicated and the titration requires care and skill in manipulation, this method gives satisfactory results if properly carried out. No difficulty arises from the presence of HCl, nor is the titration affected by the turbidity of the solution. As in other drop end-titrations, blank titration should be made under conditions identical with those of the determination, and the volume of the $\frac{N}{10}$ dichromate V.S. consumed in the blank allowed for.

23. DETERMINATION OF GLYCERIN. (Dichromate Method.)

Glycerin is oxidized to CO_2 and water, with an excess of standard potassium dichromate V.S., and the unconsumed chromate found by titration with standard ferrous salt solution. Substances reducing $K_2Cr_2O_7$ must, of necessity, be absent.

Volumetric solutions employed: Standard ammonium ferrous sulphate V.S., 3 per cent., and standard potassium dichromate V.S. (Hehner's solution), containing 74.86 Gm. of pure $K_2Cr_2O_7$ in 1000 Cc. When the dichromate is not chemically pure the exact strength of its solution is established by titration with the standard ammonium ferrous sulphate V.S.

Indicator: Potassium ferricyanide solution.

Of a sample of glycerin 0.2 Gm. are carefully weighed or a convenient volume of an aqueous solution containing as much is measured into a beaker or flask, diluted with boiled distilled water to

measure about 15 Cc. 15 Cc. of concentrated sulphuric acid are stirred in, 30 to 40 Cc. of the standard solution of dichromate, accurately measured, are added, and the mixture heated, during two hours, in a covered vessel. It is best to heat in a flask under return condenser. When the reaction is ended the cooled solution is diluted with recently boiled distilled water to a definite volume, and aliquots of it are titrated with the standard ammonium ferrous sulphate V.S. The titration is carried out in the manner given for determination of ferrous salts with $\frac{N}{10}$ dichromate V.S., the end-reaction being indicated when a drop of the titrated liquid, taken out and mixed with a drop of the indicator, is found to give a distinct blue color appearing immediately. From the volume of the standard dichromate V.S. consumed, the percentage of glycerin in sample is calculated. 1 Cc. of the standard potassium dichromate V.S. = 0.01 Gm. of glycerin.

$$3C_3H_8O_3 + 7K_2Cr_2O_7 + 28H_2SO_4 = 7K_2SO_4 + 7Cr_2(SO_4)_3 + 40H_2O + 9CO_2.$$
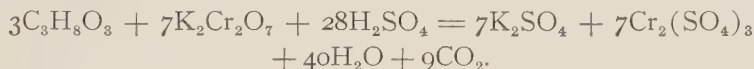
For crude glycerin, or impure solutions of it, the method of Richardson and Jaffé (J. S. Chem. Ind., 1898, 4, 330) employs lead subacetate for purification. To 25 Cc. of the sample of a weak solution, diluted with 50 Cc. of water, and neutralized, if necessary, solution of lead subacetate, 25 per cent., is added in slight excess, the mixture well agitated by shaking, filtered, and the precipitate washed with 150 Cc. of cold water. In the filtrate the excess of lead is precipitated with diluted sulphuric acid, the liquid diluted to measure 250 Cc., and 20 Cc. = 2 Cc. of the sample are drawn off for oxidation. To each such portion is added 25 Cc. of the standard dichromate V.S., 25 Cc. of concentrated sulphuric acid stirred in and the mixture heated 20 minutes on boiling water-bath, or until the oxidation is completed. The liquid is then diluted with boiled distilled water to measure 250 Cc. and titrated in 20 Cc. portions with the standard ammonium ferrous sulphate V.S. as above.

A serious objection to this method is the reactibility of potassium dichromate. Phosphates and chlorides are objectionable. Aldehydes and chlorides may be removed with moist Ag_2O acting 10 minutes.

The factor derived by Hehner has been found low by F. Schulze (Chem. Zeit., 1905, 29, 976), who says that 74.86 Gm. of potassium dichromate oxidize more nearly 11 Gm. of glycerin so that 1 Cc. of the V.S. corresponds to 0.011 Gm. of glycerin.

II. INDIRECT OXIDATION METHODS.
Direct Titrations.

24. DETERMINATION OF THIOSULPHATES.

Thiosulphate is oxidized by iodine to tetrathionate.
Volumetric solution employed: $\frac{N}{10}$ iodine.
Dissolve about 0.5 Gm. of sample, accurately weighed, in 20 Cc. of water and titrate the solution with the $\frac{N}{10}$ iodine V.S. Run the V.S.

into the solution of the sample from a burette in small portions, mixing well after each addition.   Reduce the flow to drops toward the end of the titration, that is, when the yellow color produced by the added iodine begins to disappear less rapidly, and continue the addition carefully until finally one drop of the V.S. produces a distinct, permanent yellow color.   Having confirmed the result by a check titration, calculate the percentage of the thiosulphate present in the sample.   The factor for sodium thiosulphate with $\frac{N}{10}$ iodine is 0.024824 Gm. and is derived from the equation:

$$\underset{2 \times 248.24}{2N_2S_2O_3 \cdot 5H_2O} + \underset{2 \times 126.92}{2I} + 2NaI + Na_2S_4O_6 + 10H_2O.$$
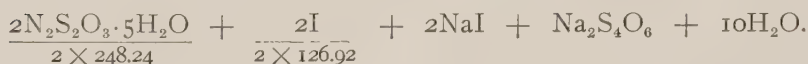
This shows that 126.92 parts of iodine react with 248.24 parts of Na thiosulphate.

1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 24.824 Gm. $Na_2S_2O_3 \cdot 5H_2O$.

1 Cc. is, therefore, the equivalent of 0.024824 Gm. of sodium thiosulphate.

To calculate the percentage:

$$\frac{Cc. \text{ V.S. consumed} \times 0.024824 \times 100}{\text{Weight of sample}} = \text{per cent. sod. thiosulphate.}$$

Observation.—Since the factor is derived for a thiosulphate containing water of crystallization, the sample used for analysis must be crystalline and the crystals uneffloresced, otherwise high values will be obtained even when the sample contains considerable impurities.

25. Determination of Sulphites and Bisulphites.

These salts of sulphurous acid are oxidized by iodine to sulphates. In titration some neutralizing agent ($NaHCO_3$) must be present to combine with HI formed.

Volumetric solution employed: $\frac{N}{10}$ iodine.

Employ 0.2 to 0.4 Gm. of the sample for one titration.   Weigh accurately, dissolve in 20 Cc. of water, add 1 Gm. of $NaHCO_3$ and titrate with the $\frac{N}{10}$ iodine V.S. as in the case of the thiosulphate. When one drop of the V.S. is found to have imparted to the titrated liquid a distinct, permanent yellow color, the oxidation is completed. Having made a check titration, calculate the percentage of the particular salt in the sample.

In the case of sodium sulphite, the reaction with iodine is represented in the following equation which serves to derive the required factor:

$$\underset{252.2}{Na_2SO_3 \cdot 7H_2O} + \underset{2 \times 126.92}{2I} = Na_2SO_4 + 2HI + 6H_2O.$$
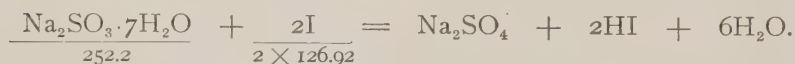
126.97 parts of iodine react with $\frac{252.2}{2} = 126.1$ parts of sodium sulphite.

1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 12.61 Gm. $Na_2SO_3 \cdot 7H_2O$.

1 Cc. is, therefore, the equivalent of 0.01261 Gm. of crystalline sodium sulphite.

Factors for other sulphites and bisulphites are found in like manner. The secondary reaction:

$$HI + NaHCO_3 = NaI + CO_2 + H_2O,$$
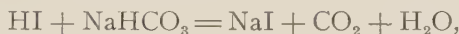
in which the HI formed is neutralized, is not considered in the calculation.

Observations.—The function of $NaHCO_3$, represented in the equation, has been discussed under standardization of $\frac{N}{10}$ iodine V.S. by tenth-normal arsenous acid V.S., *q. v.* Sulphides and bisulphides may also be determined by residual titration (U.S.P. method). To 50 Cc. of the $\frac{N}{10}$ iodine V.S. contained in a glass-stoppered bottle of 100 Cc. capacity, 0.5 Gm. of the sample is added, the bottle closed and contents mixed well by shaking. In the case of the sulphites the titration is made as soon as the sample has dissolved, while with bisulphites 1 hour should be allowed, with frequent shaking, for complete oxidation. If the solution be colored, starch solution should be used as indicator.

26. DETERMINATION OF SULPHUROUS ACID.

Sulphurous acid is oxidized with an excess of standard iodine and the excess of the latter titrated with standard thiosulphate.

Volumetric solutions employed: $\frac{N}{10}$ iodine and $\frac{N}{10}$ thiosulphate.

Into a titration flask measure exactly 50 Cc. of $\frac{N}{10}$ iodine V.S., add 2 Cc. of the sample and let stand 3 to 4 minutes. Titrate the unconsumed iodine with $\frac{N}{10}$ thiosulphate V.S., adding this in small portions and mixing well after each addition. When the brown color of the titrated liquid changes to yellow, reduce the flow to drops and continue to add one drop at a time until one drop finally discharges the light yellow color. Carry out a check titration and, from the results, calculate the percentage of the acid in sample. The volume of the $\frac{N}{10}$ iodine consumed by the sulphurous acid is found by subtracting the volume in Cc. of $\frac{N}{10}$ thiosulphate consumed from 50 Cc., the volume of $\frac{N}{10}$ iodine used. To find the weight of 2 Cc. of the sample which must be had for the calculation of percentage, exactly 2 Cc. are measured into a small glass-stoppered weighing flask and accurately weighed.

The reactions involved are represented by the equations from which the factor for sulphurous acid is derived:

$$\underset{64.07}{SO_2} + \underset{2 \times 126.92}{2I} + 2H_2O = H_2SO_4 + 2HI.$$

$$I_2 + \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} = 2NaI + Na_2S_4O_6 + 10H_2O.$$

10
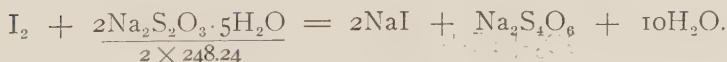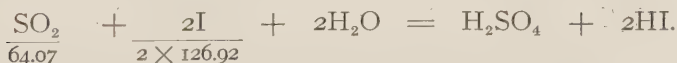
It appears that 126.92 parts of iodine react with 32.035 parts of SO_2, then,

1 Lt. of $\frac{N}{10}$ iodine containing 12.692 Gm. corresponds to 3.2035 Gm. of SO_2, and

1 Cc. of the V.S. is, therefore, the equivalent of 0.0032035 Gm. of sulphurous anhydride.

Observations.—The titration is made residual and the acid added to the $\frac{N}{10}$ iodine V.S. to prevent loss by volatilization and to avoid incomplete oxidation with separation of sulphur which takes place, when the iodine solution is run into the sulphurous acid, according to the equation:

$$SO_2 + 4HI = S + 4I + 2H_2O.$$

When other iodine-consuming substances such as the sulphites or the organic compounds, phenol, gallic acid, tannin, etc., are present, the acid should be distilled into an excess of standard iodine V.S., and the excess titrated with the thiosulphate V.S. For this purpose the air within the distilling apparatus is displaced by CO_2 and, after most of the SO_2 has been distilled over, the remaining traces of the gas are carried over by a slow current of CO_2. To guard against loss of iodine another absorption flask containing KI solution or a measured volume of $\frac{N}{10}$ thiosulphate V.S. is attached to the receiver containing the $\frac{N}{10}$ iodine. The two absorption solutions are mixed before the titration of the excess of the iodine is commenced. If $\frac{N}{10}$ thiosulphate V.S. were used in the guard tube and, on addition to the iodine in the receiver, the iodine is decolorized, the titration must be completed with $\frac{N}{10}$ iodine, otherwise the volume of the thiosulphate is subtracted from that of iodine placed in the receiver.

A simple titration of a measured volume of $\frac{N}{10}$ iodine, with the sulphurous acid solution may be made, and, from the volume of the acid required to decolorize the iodine, the percentage of the acid present is calculated.

27. Determination of Sulphite and Thiosulphate, Present Together.

Sulphites do not react with mercuric chloride, while a thiosulphate is decomposed, giving sulphide and a sulphate. The thiosulphate may, therefore, be decomposed with an excess of mercuric chloride and, in the filtrate, the sulphite present determined by decomposing it with an acid and distilling the SO_2 into standard iodine. To represent the reactions:

$$Na_2S_2O_3 + HgCl_2 + H_2O = Na_2SO_4 + HgS + 2HCl.$$

$$Na_2SO_3 + 2HCl = 2NaCl + SO_2 + H_2O.$$

$$SO_2 + 2I + 2H_2O = H_2SO_4 + 2HI.$$
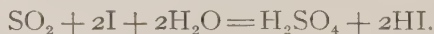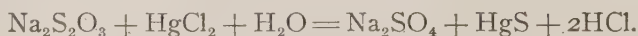
The decomposition and subsequent distillation should be made in an air-tight apparatus containing CO_2, the last traces of the SO_2 being carried over by a current of CO_2. To prevent loss of iodine a guard "U"-tube containing KI solution or $\frac{N}{10}$ thiosulphate (a measured volume) is attached to the receiver. The volume of the $\frac{N}{10}$ iodine V.S. consumed by the SO_2 is employed in calculation of the percentage of the sulphite present. The thiosulphate is found, by difference; a separate titration of a portion of the sample gives the volume of $\frac{N}{10}$ iodine that corresponds to both the sulphite and thio-sulphate. The difference of the two volumes of $\frac{N}{10}$ iodine V.S. corresponds to the thiosulphate.

28. THIOSULPHATE IN PRESENCE OF SULPHITE.

Where the above methods can not be employed another one, based on the reaction of tetrathionate with nascent hydrogen in which H_2S is formed, is utilized. In a suitable quantity of the sample both salts are oxidized by titration with standard iodine V.S., starch solution being used as indicator, and the V.S. added until one drop of it just produces a distinct blue color. The reactions are represented:

$$Na_2SO_3 + 2I + H_2O = Na_2SO_4 + 2HI.$$

$$2Na_2S_2O_3 + 2I = Na_2S_4O_6 + 2NaI.$$
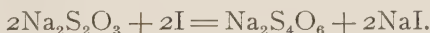
For the reduction of the tetrathionate $Al + HCl$ are added to the cold oxidized solution, diluted with 50 Cc. of water, and the H_2S generated, distilled by gentle heating into an excess of $\frac{N}{10}$ iodine V.S. The unconsumed iodine is then titrated with $\frac{N}{10}$ thiosulphate in presence of sodium bicarbonate as in determination of hydrogen sulphide, iodometrically (see 29), or the gas may be passed into an excess of ferric sulphate, and the ferrous sulphate produced titrated with standard permanganate V.S. as in the Mohr method.

$$Na_2S_4O_6 + 6Al + 20HCl = 4H_2S + 2NaCl + 6AlCl_3 + 6H_2O.$$

$$H_2S + 2I = 2HI + S.$$
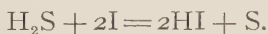
Sulphide, when present, is removed by addition of cadmium carbonate.

29. DETERMINATION OF HYDROGEN SULPHIDE AND THE SOLUBLE SULPHIDES.

Hydrogen sulphide is decomposed by iodine with production of HI and separation of sulphur.

Volumetric solution employed: $\frac{N}{10}$ iodine.

Indicator: Starch solution.

Into an excess of sodium bicarbonate (about 20 Cc. of the cold, saturated solution) contained in a half-liter flask, measure a suitable volume of the sample of the hydrogen sulphide solution or that of a sulphide containing about 0.2 Gm., close the flask and mix the con-

tents well.   Dilute with 300 to 400 Cc. of water, add 2 Cc. of starch·
solution and titrate with the $\frac{N}{10}$ iodine V.S. to the production of a
distinct and permanent blue color.   For calculation, the average
of at least two closely agreeing titrations should be used.   The
factor for H_2S with $\frac{N}{10}$ iodine V.S. is 0.0017045 Gm. and is derived
from the equation:

$$\underset{34.09}{H_2S} \quad + \quad \underset{2 \times 126.92}{2I} \quad = \quad S \quad + \quad 2HI.$$
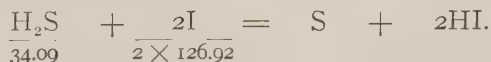
Of iodine, 126.92 parts react with 34.09 parts of hydrogen sul-
phide, and as 1 Lt. of $\frac{N}{10}$ iodine containing 12.692 Gm., corresponds
to 1.7045 Gm. of H_2S,

1 Cc. of the V.S. is the equivalent of 0.0017045 Gm. of hydrogen
sulphide.

Observations.—Though the results of this titration are not affected
by the presence of the separated sulphur, the end-point is made
sharper if the liquid is largely diluted.   When much sulphur sepa-
rates in a concentrated solution it is apt to hold iodine.   By shaking
with carbon disulphide the separated sulphur may be effectively
removed.   The titration of H_2S is often made residual, the sample
being added to an excess of standard iodine V.S., mixed with
$NaHCO_3$ solution, and, after thorough mixing, the excess of iodine
titrated with standard thiosulphate V.S.   In the presence of sub-
stances which react with iodine, H_2S is distilled into an excess of
standard iodine V.S.

Insoluble sulphides may be converted into soluble salts by boiling
with $NaOH$ and saturating the solution, after filtration, with CO_2,
and titrating.

Sulphides, decomposable by dilute acids, are heated with 10 per
cent. HCl in a flask, connected with another flask, or any other
form of absorption vessel containing an excess of standard iodine,
carefully measured.   The H_2S set free by the acid is distilled into
the iodine and, after the gas in the apparatus has been carried over
by a current of CO_2, the unconsumed iodine is titrated with standard
thiosulphate V.S.   To prevent loss of the standard iodine the
absorption vessel containing it should be kept cool and a guard
tube containing KI solution, or a standard thiosulphate V.S., at-
tached to it to prevent loss of iodine.   For titration, the contents
of the two vessels are combined, and if the thiosulphate should
decolorize the iodine, titration is completed with $\frac{N}{10}$ iodine V.S.

For small quantities of H_2S (in mineral water) $\frac{N}{100}$ iodine should
be employed and 1000 Cc. of the sample shaken with a measured
volume of it in a glass-stoppered cylinder, the excess of iodine being
then titrated with $\frac{N}{100}$ sodium thiosulphate V.S.   However, such
small quantities of H_2S are best determined colorimetrically.

30. Determination of Arsenous Compounds.

"Arsenous" compounds are oxidized to "arsenic" by iodine.
The reaction is reversible so that the titration must be carried out
in the presence of a suitable neutralizing agent for HI to prevent
it reacting.

Volumetric solution employed: $\frac{N}{10}$ iodine.

Indicator: Starch solution.

(a) *In Arsenic Trioxide, Arsenous Iodide and the Arsenites.*— Take for each titration from 0.1 to 0.25 Gm. of the sample and, having weighed accurately, dissolve it in 25 Cc. of water. To dissolve the oxide, add NaOH solution and warm, cool the resulting solution and subsequently saturate with CO_2. When the solution is acid, neutralize, add 1 Gm. of $NaHCO_3$ and, if colorless, titrate without the indicator, proceeding as given for the titration of a thiosulphate. A distinct, permanent yellow color should be imparted by one drop of the V.S., finally added, to the titrated liquid. When the solution of the sample is colored, add 1 Cc. of the starch solution and titrate carefully, mixing well, until one drop of the V.S. finally produces a distinct, permanent blue color. Carry out a check titration and, from the results obtained, calculate the percentage of the arsenous compound in the sample. To represent the reaction the following equation will serve as a typical example:

$$\underset{198}{As_2O_3} \quad + \quad 2H_2O \quad + \quad \underset{4 \times 126.92}{4I} \quad = \quad As_2O_5 \quad + \quad 4HI.$$
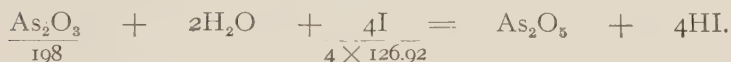
As represented, 126.92 parts of iodine react with $\dfrac{198}{4} = 49.95$ parts of As_2O_3.

1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 4.95 Gm. of As_2O_3.

1 Cc. of the V.S. is, therefore, the equivalent of 0.00495 Gm. of arsenic trioxide.

The secondary reaction:

$$HI + NaHCO_3 = NaI + H_2O + CO_2,$$
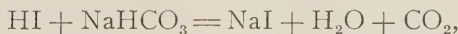
is not considered in the calculations.

(b) *In Solution of Potassium Arsenite, Arsenous Acid, etc.*— Transfer to a weighing bottle 10 to 20 Cc. of the sample, weigh accurately, dilute to 25 or 30 Cc. with water, neutralize if need be, add 1 Gm. of $NaHCO_3$ and titrate with the $\frac{N}{10}$ thiosulphate V.S., as above, using 1 Cc. of a cold starch solution for colored solutions.

Observations.—If it should be desired to use starch solution as indicator in titration of colorless samples, the end-point is best indicated when only a pink color is produced by the final drop of the V.S. For very accurate titrations standard tints, prepared by mixing solutions of certain colored salts, such as ferric chloride, cobalt nitrate and copper sulphate, have been recommended by Washburn.[1] Three such tints may be made. The lightest one is prepared by mixing these solutions in such proportions as to obtain a color that will exactly match the tint which one drop of $\frac{N}{100}$ iodine produces with a given quantity of water and 1 Cc. of starch solution. The second, deeper tint, is made to correspond to 2 drops of the

[1] J. A. Chem. Soc., 1908, 1, 31–46.

$\frac{N}{100}$ iodine; the third, to 3 drops.   To be accurate, the titration is completed with $\frac{N}{100}$ iodine and the end-point made to match one of the prepared tints, or, the standard tints are used to approximate, by comparison, the quantity of the $\frac{N}{100}$ V.S. added in excess.   Since the volume of $\frac{N}{100}$ iodine required to produce any one of these tints is known, any intermediate tint is readily approximated and the necessary correction made.

Sodium phosphate, Na_2HPO_4 may be used in place of the bicarbonate to fix the HI.   The proportion of sodium phosphate recommended is 0.11 Gm. of $Na_2HPO_4 \cdot 12H_2O$, for 1 Cc. of $\frac{N}{10}$ iodine consumed.   There being a loss of CO_2 in this titration, a current of the gas should be passed through the solution, or few drops of diluted acid added.

31. Determination of Antimony and Potassium Tartrate.

Antimonous compounds are oxidized to antimonic by iodine.   The reaction being a reversible one the HI produced must be neutralized as soon as formed.

Volumetric solution employed: $\frac{N}{10}$ iodine.

Indicator: Starch solution.

From 0.4 to 0.5 Gm. of the sample will be a suitable quantity for one titration.   Weigh accurately, dissolve in 20 Cc. of water, heating if need be, cool, add 20 Cc. of a cold saturated solution of $NaHCO_3$, 1 Cc. of starch solution, mix, and at once titrate with the $\frac{N}{10}$ iodine V.S.   Add the V.S. rather rapidly, mixing the titrated liquid well and continue the addition without unnecessary interruption until one drop produces a permanent blue color.   From the average of two or more agreeing results calculate the percentage of the tartar emetic, or Sb, in the sample.   The factor for calculation of the percentage of antimony and potassium tartrate with $\frac{N}{10}$ V.S. is 0.01668 Gm. and is derived from the equation:

$$\frac{2KSbOC_4H_4O_6 \cdot H_2O}{664.7} \quad + \quad 2H_2O \quad + \quad \frac{4I}{4 \times 126.92}$$
$$= \quad 4HI \quad + \quad 2KHC_4H_4O_6 \quad + \quad 2SbHO_3.$$
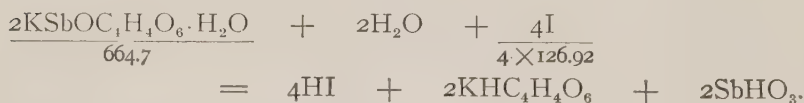
126.92 parts of iodine react with

$$\frac{664.7}{4} = 16.618 \text{ Gm. of } KSbOC_4H_4O_6,$$

and, since, 1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 16.618 Gm. $KSbOC_4H_4O_6$,

1 Cc. of the V.S. is, therefore, the equivalent of 0.016618 Gm. of antimony and potassium tartrate or of 0.00601 Gm. of antimony.

To calculate:

$$\frac{\text{Cc. of V.S. cons.} \times 0.016618 \times 100}{\text{Weight of sample}} = \text{per cent. antim. and pot. tar.}$$

The secondary reaction:

$$HI + NaHCO_3 = NaI + CO_2 + H_2O,$$
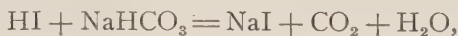
is not considered in the calculation.

Observations.—Titration with standard iodine must be rapid, in order that antimonous hydroxide should not precipitate, the separated compound not being readily acted on by iodine. The end-point in this titration is not very sharp, a gradation of tints appearing before the desired blue is produced. To obtain accurate results the iodine V.S. should be standardized with a standard antimony and potassium tartrate solution and the titration in determinations carried out in the same manner and to the same shade of color of the end-reaction as in the standardization.

32. Antimony in other Antimonous Compounds.

The oxide or oxychloride, when free from antimonic compounds, is dissolved in HCl, the free acid nearly neutralized with NaOH, 1 to 2 Gm. of sodium and potassium tartrate added, then an excess of $NaHCO_3$ (about 3 Gm.), and the solution titrated as in 31. When antimonic compounds or other oxidizable substances are present, antimony is separated as Sb_2S_3 by a current of H_2S passed into the acidified solution, the precipitate is washed, dried, dissolved in HCl, the solution heated to remove H_2S, any separated S filtered off, the acid neutralized, $NaHCO_3$ added and the liquid titrated with standard iodine V.S. Instead of dissolving in HCl the sulphide may be dissolved in K_2S, the solution evaporated with $KHSO_4 + H_2SO_4$, the residue taken up with HCl, neutralized and titrated. Antimony in alloys is usually separated as the sulphide by ammonium sulphide and the sulphide treated as above. Tartaric acid or the soluble tartrates are used to keep the oxide or oxychloride in solution; salts which they fail to keep in solution are evaporated with $KHSO_4 + H_2SO_4 + $ tartaric acid to dryness, the residue taken up with HCl and, after neutralization, titrated.

33. Determination of Reduced Iron.

The reduced iron is dissolved in excess of strong solution of iodine and the unconsumed iodine titrated with standard thiosulphate V.S. Volumetric solution required: $\frac{N}{10}$ thiosulphate.

To carry out the determination, weigh accurately into a 100-Cc. flask about 2 Gm. of iodine, the purity of which is to be determined by titration of another portion, add 5 Cc. of water, then 2 Gm. of KI, free from iodate, and introduce from 0.3 to 0.4 Gm. of the sample, also carefully weighed. Close the flask with a stopper, mix the contents well, shaking at intervals during 1 hour. When all iodine is dissolved, dilute to a convenient, but definite volume, and titrate in aliquot portions with the $\frac{N}{10}$ thiosulphate, adding the V.S. so that one drop of it will discharge the final yellow color of iodine in the titrated liquid. From the volume of $\frac{N}{10}$ thiosulphate V.S. required to react with the iodine consumed by the iron, or

from the quantity of iodine so consumed, calculate the percentage of Fe in the sample. The reactions on which the calculation is based are represented:

$$\frac{Fe}{55.85} + \frac{I_2}{2 \times 126.92} = FeI_2.$$

$$2I + 2Na_2S_2O_3 \cdot 5H_2O = 2NaI + Na_2S_4O_6 + 10H_2O.$$
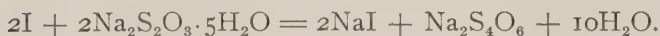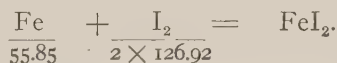
55.85 parts of iron consume 2×126.92 parts of iodine, and the equivalent of 1 Cc. of $\frac{N}{10}$ thiosulphate V.S. is 0.012692 Gm. of iodine.

Having found, by titration of another portion, the quantity of absolute iodine present in the portion of the iodine used for the sample, and subtracting from it the quantity which corresponds to $\frac{N}{10}$ thiosulphate V.S. consumed by the excess, employ the difference, representing iodine consumed by the iron in the sample, for calculation of percentage. The proportion becomes:

$$(2 \times 126.92)\ 253.84 : 55.85 :: I \text{ consumed by } Fe : x.$$

$$x = \frac{55.85 \times I \text{ consumed by } Fe \times 100}{253.84 \times \text{Weight of sample}} = \text{per cent. of Fe in sample.}$$

34. Determination of Tin.

Like the antimonous compounds, stannous salts ($SnCl_2$) are titrated with standard iodine in the presence of a tartrate and bicarbonate. The tin salt is dissolved in water and dilute HCl, the metal in HCl in an atmosphere of CO_2. Of the metal 0.1 Gm. will be found a sufficient quantity, while 0.3 Gm. of the salt may be used. One (1) gramme of tartaric acid is added, the solution made alkaline with NaOH, CO_2 passed in to saturation, some $NaHCO_3$ (1 to 2 Gm.) added and the liquid titrated with $\frac{N}{10}$ iodine, using starch solution as indicator.

1 Cc. of $\frac{N}{10}$ iodine corresponds to 0.00595 Gm. of Sn.

For more exact results the iodine V.S. should be standardized with pure tin, the method of solution and titration employed in the determination being closely followed.

C. Titrations with Standard Sodium Thiosulphate V.S.
(Iodometric Methods).

By direct titration only uncombined iodine, seldom chlorine or bromine, may be determined, but many substances may be determined by titration of the iodine which they liberate from soluble iodides. Since the iodine set free by the substances determined, constitutes an equivalent amount, the volume of standard thiosulphate V.S. required for its combination serves as a measure of the quantity of the iodine-liberating substance present. These substances are thus determined indirectly. The direct and indirect titrations may be simple or residual. In the residual titrations

two V.S. are used, the excess of one being titrated with the other. In these methods the end-point is sharper and more easily observed if the titration is completed with standard iodine V.S.

1. Direct Titrations.

35. Determination of Iodine.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

(a) *In Solution of Iodine or a Sample of Iodine.*—Of the solution employ for each titration from 5 to 10 Cc., of the sample of iodine 0.2 to 0.4 Gm., weighing accurately, each in a tared glass-stoppered weighing bottle. Dissolve the iodine in a strong solution of pure potassium iodide. In either case dilute to 25 Cc. with water, and titrate with the $\frac{N}{10}$ thiosulphate V.S. Add the V.S. in small portions, mixing well after each addition, and when the brown color of the titrated liquid changes to yellow, reduce the flow to drops and continue to add drop at a time until one drop of the V.S. is found to discharge the final, light yellow color. Confirm the result obtained by a check titration and, from the volume of the V.S. consumed, calculate the percentage of iodine in the sample. The factor for iodine with $\frac{N}{10}$ V.S. is 0.012692 Gm. and is obtained from the following equation:

$$\underset{2 \times 126.92}{2I} + \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} = 2NaI + Na_2S_4O_6 + 10H_2O.$$
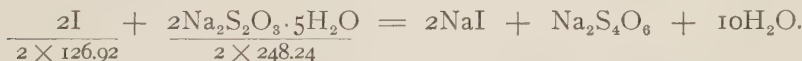
It is seen that 248.24 parts of the thiosulphate react with 126.92 parts of iodine.

1 Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to 12.692 Gm. iodine.

1 Cc. of the V.S. is, therefore, the equivalent of 0.012692 Gm. of iodine.

To calculate percentage:

$$\frac{\text{Cc. of V.S. consumed} \times 0.012692 \times 100}{\text{Weight of sample}} = \text{per cent. iodine.}$$

(b) *In Tincture of Iodine.*—Measure from an all-glass burette or by means of a pipette, 5 Cc. of the sample, into a titration flask, dilute with water to 25 or 30 Cc., and titrate with the $\frac{N}{10}$ thiosulphate V.S. as given for the solution of iodine. The factor is here of course the same as there, but the results are not calculated as percentage, the iodine found being expressed in Gm. per 100 Cc.

Illustration.—A tincture of iodine, titrated in 5 Cc. portions, required as an average of three titrations, 27.75 Cc. of $\frac{N}{10}$ thiosulphate V.S.; to calculate the quantity of iodine in 100 Cc. of the tincture.

$$27.75 \times 0.012692 = 0.35220 \text{ Gm. of iodine in 5 Cc.}$$

$$5 : 0.35220 :: 100 : x.$$

$$x = \frac{0.35220 \times 100}{5} = 7.04.$$

The tincture is found to contain 7.04 Gm. of iodine in 100 Cc.

Observations.—In measuring iodine solutions with a pipette, sufficient time should be allowed for draining. When a tincture of iodine contains no iodide (the old U.S.P. kind) some potassium iodide must be added to it before dilution with water is made, to prevent precipitation of the iodine. Occasionally a solution or tincture of iodine can not be completely decolorized by the standard thiosulphate. Such solutions should be largely diluted and titration performed with the aid of starch solution, which is added to the titrated liquid when the end-point is approached, that is, when the solution titrated shows only a weak, yet distinct, iodine color. The V.S. must then be added in one or two drop portions at successively longer intervals, the blue mixture being well shaken after each addition. The blue color should be finally discharged by one drop of the $\frac{N}{10}$ thiosulphate V.S.

Iodine containing Cl as ICl gives high results for iodine on account of the reaction: $ICl + KI = KCl + I_2$. Of a sample of iodine dried over $CaCl_2$, 0.4 Gm. should not consume more than 31.2 Cc. $\frac{N}{10}$ thiosulphate V.S., corresponding to 99 per cent. of iodine.

2. Indirect Titrations.

36. Determination of Free Chlorine or Bromine (in Solution).

Chlorine or bromine liberate an equivalent quantity of iodine from soluble iodides; the iodine set free is titrated with standard thiosulphate.

Volumetric solution employed: $\frac{N}{10}$ sodium thiosulphate.

To a measured volume of the solution of the sample add a solution of KI, free from iodate, and titrate with the $\frac{N}{10}$ thiosulphate V.S. The end-reaction is indicated when one drop of the V.S. is found to have discharged the final yellow color of the titrated liquid. When other iodine-liberating substances are present, distillation of the bromine or chlorine into solution of KI will have to be made, and the iodine in the receiver titrated as before. The quantity of KI required should be sufficiently large to react with all the halogen and hold the liberated iodine in solution. The factors for these elements are readily derived from the equations:

1. $\dfrac{Cl}{35.46} + KI = KCl + \dfrac{I.}{126.92}$

2. $\dfrac{Br}{79.92} + KI = KBr + \dfrac{I.}{126.92}$

3. $\dfrac{2I}{2 \times 126.92} + \dfrac{2Na_2S_2O_3 \cdot 5H_2O}{2 \times 248.24} = 2NaI + Na_2S_4O_6 + 10H_2O.$
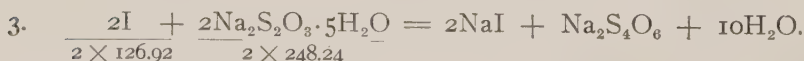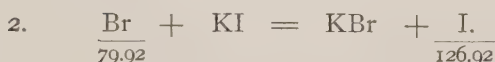
Since each element liberates an equivalent of iodine, the factor for each, with $\frac{N}{10}$ thiosulphate, is readily obtained.

35.46 parts of chlorine or 79.92 parts of bromine liberate 126.92

parts of iodine which, in return, require 248.24 parts of sodium thiosulphate for reaction.

1 Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to 3.546 Gm. chlorine, or to 7.992 Gm. bromine.

1 Cc. is the equivalent of 0.003546 Gm. chlorine, also of 0.007992 Gm. bromine.

37. DETERMINATION OF AVAILABLE CHLORINE.

(a) *In Solution of Chlorinated Soda or Chlorinated Potassa.* Carefully weigh a suitable quantity of the sample (5 Gm.), dilute with water to 50 Cc., add 2 Gm. of KI, 5 Cc. of concentrated HCl, mix well and titrate with the $\frac{N}{10}$ thiosulphate V.S. Add the V.S. in small portions first, then drop by drop, until the final yellow color of the titrated liquid is discharged by a single drop of the V.S. From the average of two or more agreeing titrations calculate the percentage of available chlorine in the sample. The factor found is for free chlorine as may be seen from the equations:

$$\underset{2 \times 35.46\,(Cl)}{Na_2OCl_2} + 2KI + 2HCl = \underset{2 \times 126.92}{2I} + 2NaCl + 2KCl + H_2O.$$

$$2I + \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} = 2NaI + Na_2S_4O_6 + 5H_2O.$$
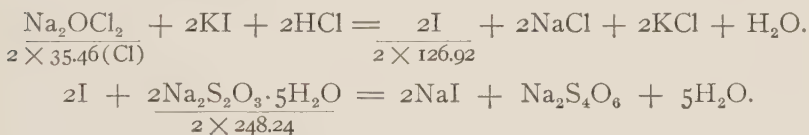
Seeing that 35.46 parts of available chlorine liberate 126.92 parts of iodine and these react with 248.24 parts of sodium thiosulphate, and that 1 Lt. $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to 3.546 Gm. of chlorine,

1 Cc. of the V.S. is, therefore, the equivalent of 0.003546 Gm. of available chlorine.

Illustration.—Several 5 Gm. portions of chlorinated soda required an average of 36.2 Cc. of $\frac{N}{10}$ thiosulphate for titration of the iodine liberated, to find the percentage of available chlorine in the sample.

$$\frac{36.2 \times 0.003546 \times 100}{5} = 2.567.$$

The sample is found to contain 2.567 per cent. of available chlorine.

(b) *In Chlorinated Lime (Bleaching Powder).*—Employ about 0.5 Gm. of the sample for each titration. Weigh accurately in a glass-stoppered weighing bottle, triturate with 10 Cc. of water, dilute the mixture to 100 Cc., then add 1 Gm. of KI, 5 Cc. of 10 per cent. HCl, and titrate with the $\frac{N}{10}$ thiosulphate V.S. When one drop of the V.S. is found to have discharged the final yellow color of the titrated liquid, the reaction is completed. From the results of two or more agreeing titrations the percentage of available chlorine is calculated just as in the case of the solutions of hypochlorites. The factor is 0.003546 Gm. available chlorine. The reaction is represented:

$$CaOCl_2 + 2KI + 2HCl = 2I + CaCl_2 + 2KCl + H_2O.$$

$$2I + 2Na_2S_2O_3 = \text{etc.}$$
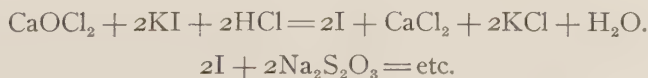
Observation.—The available chlorine becomes free by the action of the acid on the hypochlorite and in turn liberates an equivalent quantity of iodine from the iodide present. In order to keep the liberated iodine dissolved, the quantity of the iodide added must be in excess of that required to furnish the iodine. The quantity of iodine set free by the chlorine and titrated with the thiosulphate is not calculated unless specially desired, its equivalent of chlorine being at once found from the consumed thiosulphate. Colored solutions require the use of starch solution as indicator. The indicator should be added only towards the end of the titration, the approach of which is indicated by the change of the brown to a light yellow color, provided this can be seen in colored liquids.

Notes.—In the presence of a *chlorate,* which would liberate iodine from $HI(KI + HCl)$ the available chlorine is determined by residual titration with standard arsenous acid V.S.; the standard As_2O_3 solution is added in excess and the excess titrated with $\frac{N}{10}$ iodine V.S.

When, in addition to the chlorate, a *chlorite* is present, the titration is made in two parts as follows: A suitable quantity of the sample is dissolved, the solution diluted to 200 or 300 Cc., standard arsenous acid V.S. is added in excess, and the excess titrated with $\frac{N}{10}$ iodine. The As_2O_3 consumed corresponds to the hypochlorite. To another portion, the exact volume of arsenous acid V.S. required (as found in previous titration), is added, the mixture diluted to 250 Cc., heated to 95° C., acidified with few drops of sulphuric acid and titrated with standard solution of indigo, which is added rapidly until a persistent greenish color is produced. The volume of indigo solution used (the solution should contain 6 Gm. per liter and be standardized with a solution of a chlorite, the strength of which is established by standard iodine V.S.), corresponds to the chlorite. A blank titration for correction of the indigo solution should be made.

38. Hypochlorous Acid in Presence of Free Chlorine.

A measured volume of $\frac{N}{10}$ HCl is added to liberate the available chlorine in the presence of KI. After the total chlorine, free and available, has been found by titration with $\frac{N}{10}$ thiosulphate, the clear solution is titrated with $\frac{N}{10}$ alkali, using methyl orange. From the results of the two titrations the hypochlorite and free chlorine present in the sample are calculated.

$$\underset{52.47}{\underline{HOCl}} + 2KI = 2I + KCl + KOH.$$

$$Cl_2 + 2KI = 2KCl + 2I.$$
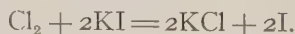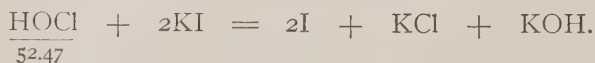
One molecule of hypochlorous acid liberates 2 atoms of iodine, one KOH being also produced. The quantity of HOCl is, therefore, readily found from the volume of $\frac{N}{10}$ acid neutralized by the KOH. Since HOCl corresponds to HCl,

1 Cc. of $\frac{N}{10}$ HCl corresponds to 0.005247 Gm. of HOCl.

If, now, twice the volume of $\frac{N}{10}$ HCl neutralized by the HOCl be subtracted from the total $\frac{N}{10}$ thiosulphate consumed, the difference

will constitute that volume of $\frac{N}{10}$ V.S. which corresponds to the free chlorine.

1 Cc. of $\frac{N}{10}$ thiosulphate corresponds to 0.003546 Gm. of chlorine.

39. DETERMINATION OF FERRIC SALTS.

(a) *The Inorganic Salts.*—Soluble ferric salts liberate iodine from soluble iodides. The volume of standard thiosulphate, which the liberated iodine requires for titration, serves to measure the quantity of the ferric salt present. It is essential that all other iodine-liberating substances be absent.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

Indicator: Starch solution.

For one titration 0.5 to 1.0 Gm. of the salt or 1 to 2 Gm. of a strong solution will be found a suitable quantity. Weigh the sample accurately, transfer to a 100-Cc. glass-stoppered bottle (if a solid, dissolve in 10 Cc. of water), and add in order: 10 Cc. of water, 5 Cc. concentrated HCl, 2 Gm. KI (free from iodate); close the bottle and warm at 40° C. during one half hour. Cool to room temperature and, having washed any iodine that may have been found adhering to the neck and stopper, into the bottle, titrate with the $\frac{N}{10}$ thiosulphate V.S. Titrate slowly, with frequent agitations of the titrated liquid, to the point when the iodine is nearly but not entirely combined, this being indicated by a change of the brown to a yellow color. Add 1 Cc. of starch solution and complete the titration with the V.S. added in successively smaller portions, that are finally reduced to drops added at longer intervals, shaking the mixture well after each addition. Finally, one drop of the V.S. should be found to discharge the blue color of the titrated liquid. Carry out a check titration and from the results obtained calculate the percentage of the particular ferric salt present in the sample.

The amount of a ferric salt present is usually expressed in terms of metallic iron, for which the factor, with $\frac{N}{10}$ V.S., is 0.005585 Gm., derived as follows:

$$\underset{344.01}{Fe_2(SO_4)_3} \;+\; 2KI \;+\; 2HCl$$

$$= \; 2FeSO_4 \;+\; H_2SO_4 \;+\; 2KCl \;+\; \frac{2I.}{2 \times 126.92}$$

$$2I \;+\; \frac{2Na_2S_2O_3 \cdot 5H_2O}{2 \times 248.24} \;=\; etc.$$
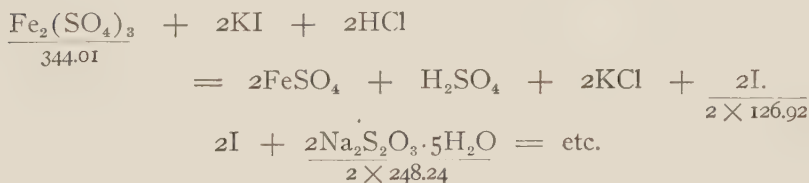
344.01 parts of ferric sulphate containing 2×55.85 parts of Fe liberate 2×126.92 parts of iodine which require 2×248.24 parts of sodium thiosulphate for combination. The relation of these equivalents then is:

$$\frac{344.01}{2}Fe_2(SO_4)_3 = 55.85 \;\; Fe = 126.92 \;\; I = 248.24 \;\; Na_2S_2O_3 \cdot 5H_2O.$$
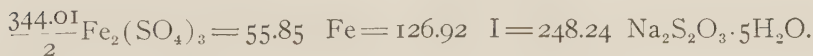
1 Lt. $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to 5.585 Gm. of Fe, so that

1 Cc. of the V.S. is the equivalent of 0.005585 Gm. of metallic iron.

To calculate:

$$\frac{\text{Cc. of V.S. cons.} \times 0.005585 \times 100}{\text{Weight of sample}} = \text{per cent. of Fe in sample.}$$

(*b*) *The Organic Salts* (*Scale Salts*).—Certain of the organic salts of iron, especially the citrate, do not readily dissolve in water, but dissolve on warming with a little ammonium hydroxide solution. Such solutions must be neutralized with HCl before the other reagents are added. These salts often contain small quantities of a ferrous salt due to a reduction during evaporation of their solutions for scaling; unless this is restored, low results will be obtained. To restore the Fe in the reduced portion to the ferric state, the solution of the sample is acidified with 5 to 10 Cc. of 10 per cent. sulphuric acid and a weak (1 per cent.) solution of potassium permanganate added until a permanent pink color is produced. The excess of permanganate is removed by a drop of oxalic acid solution and the titration of the ferric salt proceeded with as above.

Observations.—The function of HCl in these titrations is expressed in the equation:

$$KI + HCl = HI + KCl;$$

the HI being more readily decomposed by ferric compounds. Potassium iodide must be present in excess of the quantity required to furnish the iodine to be liberated, in order that this may remain dissolved. The possibility of the reverse reaction:

$$2FeCl_2 + 2I + 2HCl = Fe_2Cl_6 + 2HI$$

has been pointed out by Carcano and Namias (Bull. Chim. and Farm., 43, 54), who state that exact results can be obtained only under the following conditions: Use more of HCl and KI, dilute the solution to contain 1 to 2 per cent. of Fe and titrate in the presence of 5 to 10 Cc. of chloroform, with starch solution as indicator.

Alkaloids reacting with iodine interfere with the titration of ferric salts when present in the sample; their removal is, therefore, necessary. If the sample is to be assayed for both the alkaloid and the iron contents, the solution is transferred to a separator, made alkaline with ammonium hydroxide and the alkaloid removed by shaking out with chloroform. The chloroformic solution gives the alkaloid on evaporation, while the aqueous solution, after it is neutralized, is used for titration of the ferric salt. Should the quantity of Fe present only be sought, the alkaloid may be removed by precipitation with an excess of ammonium hydroxide; it is then filtered off and the filtrate employed for titration of the iron.

Note.—Ferrous compounds must be oxidized to ferric to be available for treatment. This may be brought about by permanganate as given in the case of the partly reduced organic salts, or by heating with an excess of HNO_3, nitro-HCl, or $KClO_3 + HCl$.

In any case the unconsumed oxidizing agent, which is used in excess, must be removed. When HNO_3 has been used for oxidation, the solution must be evaporated with HCl to near dryness, to remove HNO_3, the residue taken up with water, free acid neutralized with $NaHCO_3$, and the solution treated as directed for ferric salts. When iodine-liberating substances are present in ferric chloride, the Fe may be precipitated from the solution, with NH_4OH, the precipitate filtered, washed, dissolved in HCl, and titrated.

40. Determination of Copper.

Copper sulphate liberates iodine from soluble iodides, the iodine is titrated with standard thiosulphate.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

Indicator: Starch solution.

From 0.2 to 0.3 Gm. of the sample of copper salt will be a suitable quantity for a titration. Weigh accurately, dissolve in 10 Cc. of water in a glass-stoppered bottle, add 10 Cc. of 10 per cent. KI solution and, closing the bottle, shake well until decomposition is completed. Dilute the mixture with an equal volume of water and run in the $\frac{N}{10}$ thiosulphate until the brown color of the titrated liquid is changed to yellow; then add 1 Cc. of starch solution and complete the titration, adding the V.S. in drop portions and mixing well, so that one drop should finally discharge the blue color. For the calculation of the percentage of Cu, another titration should be made to check the first. The factor for copper with $\frac{N}{10}$ V.S. is 0.006357 Gm. and is derived from the following equations:

$$\underset{2 \times 63.57\,(\text{Cu})}{2CuSO_4} + 4KI = Cu_2I_2 + 2K_2SO_4 + \underset{2 \times 126.92}{2I.}$$

$$2I + \underset{2 \times 248.24}{2Na_2S_2O_3} = \text{etc.}$$
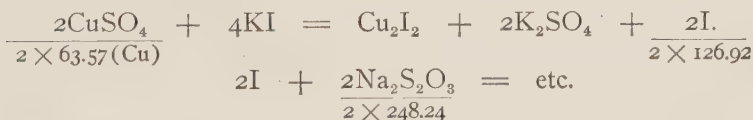
which show that 63.57 parts of Cu (as $CuSO_4$) react with 126.92 parts of I which, in turn, consume 248.24 parts of sodium thiosulphate. Since 1 Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to 6.357 Gm. of copper,

1 Cc. must correspond to 0.006357 Gm. of metallic copper.

Observations.—The solution of the sample must be neutral or only weakly acid. Nitrates and other iodine-liberating substances, as well as interfering metals (Pb, Bi, Fe, As, Sb, etc.), must be absent. When nitrate of copper which is usually had in separations of copper from other metals is to be treated, the nitrate ions (NO_3) will be made harmless if combined with an alkali metal, and the inorganic acids are excluded. This is accomplished, according to Low, by adding ammonium hydroxide to the copper nitrate solu-

tion until a clear blue solution results, heating to 100° C., boiling a minute and acidifying strongly with acetic acid. The acid solution is diluted with water, KI added and titration carried out as above.

Note.—To obtain reliable results with this method the $\frac{N}{10}$ thiosulphate V.S. should be standardized by titration with a standard solution of $CuSO_4$ prepared by dissolving pure metallic copper (electrolytic) in nitric acid and titrating the solution with that of sodium thiosulphate as in the determination. Usually 0.1 to 0.2 Gm. of the metal are dissolved in a sufficient quantity of HNO_3, the solution evaporated to 3 Cc., the residue taken up with water, ammonium hydroxide added, the liquid boiled, acidified with acetic acid and titrated. The value of 1 Cc. of the thiosulphate V.S., in terms of Cu is then readily found and used as the factor in calculation of its percentage present.

41. DETERMINATION OF MERCURY IN MERCURIC SALTS (E. RUPP).[1]

Mercury is precipitated by formaldehyde, dissolved in an excess of standard iodine solution, the excess of which is ascertained by titration with standard thiosulphate V.S.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate and $\frac{N}{10}$ iodine.

Indicator: Starch solution.

Weigh about 0.2 Gm. of the mercuric salt accurately, dissolve in 20 Cc. of water with enough KI (1 to 2 Gm.) added to obtain a clear solution. Make the solution alkaline with NaOH (5 Cc. of a 10 per cent. solution), add 2 to 3 Cc. of 40 per cent. formaldehyde solution, dilute with 10 Cc. of water and shake, warming on water-bath, if necessary, until complete reduction has taken place (about 5 minutes). Acidify with acetic acid, add an excess (30 Cc.) of $\frac{N}{10}$ iodine and mix well until the mercury is all dissolved. Add 10 Cc. of acetic acid, 2 Cc. of starch solution and titrate with the $\frac{N}{10}$ thiosulphate added slowly, with vigorous agitation of the titrated liquid, until the blue color is just discharged. Check this by another titration and, from the results, calculate the percentage of Hg in the sample. Calculation is based on the volume of $\frac{N}{10}$ iodine consumed by the mercury, and the factor required is found from the equation:

$$\frac{Hg}{200} + \frac{2I}{2 \times 126.92} = HgI_2.$$

Since 126.92 parts of iodine react with 100 parts of mercury, and 1 Lt. of $\frac{N}{10}$ iodine containing 12.692 Gm., corresponds to 10 Gm. of Hg, then

1 Cc. of $\frac{N}{10}$ iodine corresponds to 0.0100 Gm. of metallic mercury, also to 0.013546 Gm. of mercuric chloride, or to 0.012604 Gm. of mercuric cyanide.

Observations.—Concentration of the reagents and the time of reaction should not be greatly increased since HI, which would be formed, would react with the formaldehyde. Ammoniated mercury must be dissolved in KI solution.

[1] Arch. der Pharm., 1905, 300.

J. A. Mueller gives this method with the following modifications: After adding formaldehyde the mixture is allowed to stand 24 hours, the liquid decanted, mercury washed with alcohol by decantation, air is blown through the flask to remove any HCOH, standard iodine V.S. is added in excess and when Hg has all dissolved the uncombined iodine titrated with standard thiosulphate V.S. Mercurous compounds, to be assayed by this method, must be changed to mercuric, their oxidation being effected with nitrohydrochloric acid or with $KClO_3 + HCl$, the excess of oxidizing agent being carefully removed. Insoluble Hg compounds, ores, sulphide, etc., are digested with aqua regia, evaporated to dryness, KI added and the solution treated as above.

42. DETERMINATION OF MAGNESIUM (MEADE).[1]

Magnesium ammonium arsenate liberates iodine from soluble iodides in acid solutions; the iodine set free is titrated with standard thiosulphate.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

A small quantity of the sample is carefully weighed, dissolved to make a saturated solution, or, if a solution (sample of water) be had, 500 Cc. are evaporated, acidified with HCl, to a small volume, one third the volume of 10 per cent. ammonium hydroxide, then 25 Cc. of a 10 per cent. solution of sodium arsenate are added, and the mixture well shaken during 2 minutes. Filter, wash the precipitate with 2.5 per cent. ammonium hydroxide until free from arsenic, dissolve it in 50 Cc. of dilute sulphuric acid (1–4) returning the solution to the precipitation flask and washing filter with hot water. Dilute the solution to 100 Cc. with water, add 10 Cc. sulphuric acid (1 to 1) 3.5 Gm. of KI and, after 5 minutes, titrate the liberated iodine with the $\frac{N}{10}$ thiosulphate. One drop of the V.S. should be found to discharge the final yellow color. From the volume of $\frac{N}{10}$ thiosulphate V.S. consumed the percentage of Mg in the sample is calculated.

$$\underset{2 \times 24.32\,(Mg)}{2MgNH_4AsO_4} + 4KI + 5H_2SO_4$$

$$= 2MgSO_4 + 2K_2SO_4 + As_2O_3 + \underset{4 \times 126.92}{(NH_4)_2SO_4 + 4I.}$$

$$2I + \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} = \text{etc.}$$
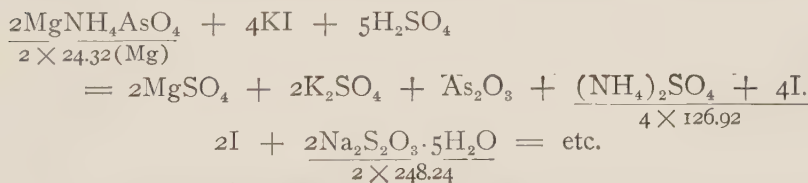
1 Cc. of $\frac{N}{10}$ thiosulphate V.S. is the equivalent of 0.001216 Gm. of magnesium, also of 0.002016 Gm. of MgO.

Note.—The determination is also carried out (Rosenthaler) by precipitating the magnesium in a portion of the sample with an excess of standard potassium arsenate, proceeding as above, making the mixture up to a definite volume with water and determining the excess of the potassium arsenate in the filtrate by titration. For this a rather large portion of the filtrate ($\frac{2}{3}$) is evaporated to

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[1] Modified by Frankforter and Cohen, J. A. Chem. Soc., 1907, 29, 1464.

dryness, taken up with the least quantity of water, transferred to a bottle provided with a well-fitting glass stopper, diluted HCl or H_2SO_4 and KI added and, after standing 15 minutes, the liberated iodine is titrated with standard thiosulphate V.S.

43. Determination of Ferrous Salts (Rupp and Horn).[1]

Ferrous compounds are oxidized to ferric by iodine in the presence of an alkali, the unconsumed iodine is then titrated with standard thiosulphate V.S.

Volumetric solutions employed: $\frac{N}{10}$ iodine and $\frac{N}{10}$ thiosulphate.

Indicator: Starch solution.

Accurately weigh 0.3 to 0.5 Gm. of the sample, dissolve in water, keeping the solution protected against oxidation. Into a glass-stoppered bottle introduce 40 Cc. of $\frac{N}{10}$ iodine V.S., add the solution of the sample and then 5 per cent. solution of NaOH until the mixture is alkaline and let stand few minutes. Acidify strongly with glacial acetic or oxalic acid, let stand 5 minutes, dilute to 100 Cc. with water and titrate the unconsumed iodine with $\frac{N}{10}$ thiosulphate V.S., adding 1 Cc. of starch solution toward the end of the titration. One drop of the V.S. should discharge the blue color of the titrated liquid. From the volume of $\frac{N}{10}$ iodine consumed in this, and a check titration, calculate the percentage of Fe present as ferrous salt in the sample. The following equations represent the changes that take place:

$$\underset{55.85\,(\text{Fe})}{FeSO_4} + 2NaOH = Fe(OH)_2 + Na_2SO_4.$$

$$2NaOH + \underset{2 \times 126.92}{2I} = NaOI + NaI + H_2O.$$

$$2Fe(OH)_2 + NaIO + H_2O = 2Fe(OH)_3 + NaI.$$

$$2I + 2Na_2S_2O_3 \cdot 5H_2O = \text{etc.}$$
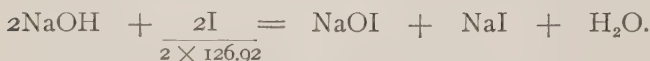
126.92 parts of iodine are seen to correspond to 55.85 parts of Fe.

1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 5.585 Gm. of iron.

1 Cc. of the V.S. is the equivalent of 0.005585 Gm. of metallic iron.

Note.—An acid must be added to liberate the iodine of the hypoiodide which forms with the alkali. Inorganic acids can not be used because the HI produced by them from KI, contained in the standard solution of iodine, would be decomposed and its iodine liberated by the ferric salt formed, the reaction being reversible. Chloride ions, if present, have no influence on the results, nor is the presence of manganese found to be objectionable. However, ammonium compounds, which react with hypoiodides, must be absent.

44. Determination of Mercury in Mercurous Chloride.

Mercurous chloride is oxidized by an excess of standard iodine and the excess titrated with standard thiosulphate V.S.

[1] Archiv. der Pharm., 1906, 571.

Volumetric solutions employed: $\frac{N}{10}$ iodine and $\frac{N}{10}$ thiosulphate.

To a suitable, accurately weighed quantity of the sample an excess of $\frac{N}{10}$ iodine V.S. is added, the mixture shaken until the mercury salt is dissolved and the uncombined iodine titrated. When the final yellow color of the titrated liquid is discharged by one drop of the V.S., the reaction is completed. The factor for Hg with $\frac{N}{10}$ iodine is found from the equation:

$$\frac{Hg_2Cl_2}{470.92} + \frac{2I}{2 \times 126.92} + 6KI = 2HgI_4K_2 + 2KCl.$$
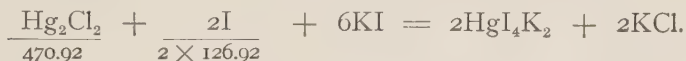
470.92 parts of $Hg_2Cl_2 = 400$ of Hg, and react with 2×126.92 parts of iodine, so that 235.46 parts $= 126.92$ parts.

1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 23.546 Gm. of Hg_2Cl_2.

1 Cc. of the V.S. is the equivalent of 0.023546 Gm. of mercurous chloride, also 0.02 Gm. of metallic mercury, and 0.02709 Gm. of mercuric chloride reduced to mercurous.

Mercuric chloride is reduced to mercurous chloride by hydrogen dioxide in the presence of HCl and tartaric acids. The acids are neutralized with 28 per cent. ammonium hydroxide, the solution acidified with tartaric acid, and 10 Cc. of the H_2O_2 added. During the next 45 minutes 15 Cc. more of the peroxide are added in 5 Cc. portions and, after standing on water-bath during 15 minutes, the mixture is filtered. The precipitate is washed, transferred to a flask, 10 Cc. of 10 per cent. KI added, then an excess of $\frac{N}{10}$ iodine, and the mixture shaken until the precipitate is dissolved. The uncombined iodine is then titrated. By this treatment mercury may be separated from As, Sb, Cd, Sn and Bi, but in the case of Bi 50 Cc. of H_2O_2 should be added during 3 hours.

45. Determination of Antimonic Compounds.[1]

Recently prepared Sb_2O_5 liberates iodine from a soluble iodide; the iodine is titrated, in acid solution, with standard thiosulphate V.S.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

Indicator: Starch solution.

The antimony sample is dissolved in nitro-HCl or HCl + Br, the excess being removed by evaporation. In a suitable quantity of the solution, acidified with HCl, the metal is precipitated as sulphide by H_2S, and, if necessary, separated from other metals by $(NH_4)_2S$. The washed sulphide is dissolved in KOH $(\frac{N}{10})$ by gentle warming and the cooled solution decolorized with 3–5 per cent. H_2O_2. The treatment is repeated with more H_2O_2 after the addition of 4 Gm. KOH for each 100 Cc. solution, and the liquid heated to boiling. When oxidation is completed, for each 100 Cc. of the liquid, 20 Cc. HCl (1.125) are added, then 1 to 1.5 Gm. pure KI introduced and, after 15 minutes, the solution titrated with $\frac{N}{10}$ thiosulphate V.S., using a little starch solution as indicator.

$$Sb_2O_5 + 4HI = Sb_2O_3 + 2H_2O + 4I.$$
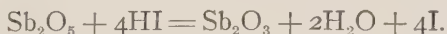
[1] Kolb & Formhals, Ztsch. anorg. Chem.. 1908, 58, 202.

1 Cc. $\frac{N}{10}$ thiosulphate is the equivalent of 0.00601 Gm. Sb.

The hydrochloric acid and water used in the operation should not contain oxygen.   Tartaric acid retards liberation of iodine.   Titration must be performed rapidly after the mixture has stood 15 minutes.   For more exact end-reaction the $\frac{N}{10}$ thiosulphate may be added in excess and titrated with $\frac{N}{100}$ iodine.

46. Determination of Chlorates, Bromates and Iodates.

Also chromic acid, chromates, dichromates, peroxide of lead (see note) and freshly precipitated MnO_2.

These compounds liberate iodine from soluble iodides in the presence of an acid; the liberated iodine is titrated with standard thiosulphate.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

Into a 100-Cc. glass-stoppered bottle introduce 0.2 to 0.3 Gm. of the sample, weighing accurately, add 1 Gm. of KI (free from iodate) and, having displaced the air in the bottle with CO_2, add 5 Cc. of strong HCl, at once close the bottle and tie the stopper down with twine.   Let the reaction proceed at room temperature which will be found sufficiently high for the decomposition of bromates, iodates and chromates.   For chlorates and the dioxides warming will be required.   This is best effected by placing the bottle in a water-bath containing cold water and heating this gradually to 60° C.   When the reaction is completed (one half hour), dilute the contents of the bottle with distilled water to 70 Cc., and titrate at once with the $\frac{N}{10}$ thiosulphate.   Add the V.S. in small portions, mixing well, and reducing the flow to drops so that one drop should discharge the final yellow color of the titrated liquid.   To find the factor for the particular compound treated, the reactions may be typically represented by the equations:

$$\underset{167.02}{KBrO_3} + 6HCl + 6KI = \underset{6 \times 126.92}{6I} + KBr + 6KCl + 3H_2O.$$

$$6I + \underset{6 \times 248.24}{6Na_2S_2O_3 \cdot 5H_2O} = \text{etc.}$$
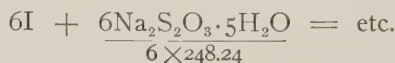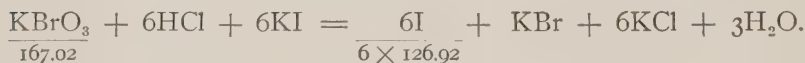
167.02 parts of $KBrO_3$ liberate 6×126.92 parts of iodine, which require for reaction, 6×248.24 parts sodium thiosulphate; one thiosulphate, therefore, corresponds to one sixth of 167.02 of potassium bromate.

1 Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to $\frac{16.702}{6} = 2.784$ Gm. of $KBrO_3$.

1 Cc. of the V.S. is the equivalent of 0.002784 Gm. of potassium bromate.

The equivalents for other bromates as well as for other compounds determined by this method of titration are similarly derived.

To calculate:

$$\frac{\text{Cc. of } \frac{N}{10} \text{ V.S.} \times 0.002784 \times 100}{\text{Weight of sample}} = \text{per cent. of } KBrO_3.$$

Notes.—Reagents containing occluded oxygen give higher results; the oxygen should be removed by boiling. For reduction, atmosphere of CO_2 is the best suited. Weak solutions of HI are more permanent than strong solution, the nonionized HI alone being acted on by the oxygen of the air. For rapid reduction of chlorates, Luther and Rutter (Ztsch. anal. Chem., 1907, 46, 521) recommend addition of 10 Cc. of $\frac{N}{10}$ solution of vanadyl sulphate ($VoSO_4$), the reduction being then brought about, at moderately high temperature, in 15 minutes. For lead dioxide (PbO_2), acetic acid, 50 per cent., is used and considerable quantity of a soluble acetate is added to prevent formation of sparingly soluble salts.

Chromate and dichromates give, on reduction, green-colored chromium salts, the color of which interferes with the end-reaction. The titration of these compounds should be completed with starch, or what is to be preferred, chloroform, as indicator (see notes on standardization of thiosulphate with $\frac{N}{10}$ dichromate, p. 102).

Hydrogen dioxide, percarbonates and persulphates may be determined iodometrically by the method given for chlorates, etc. While hydrogen peroxide requires only one half hour digestion, the percarbonates must be warmed twice as long and the persulphates should stand two hours at room temperature before titration, in order that the decomposition may be complete.

Iodate in the presence of chlorate may be determined by this method if acetic acid be used in place of HCl; in the presence of this acid, chlorate is not reduced.

This method is also available for the determination of inorganic acids such as phosphoric, etc. The iodate or bromate is used in excess, the quantity of liberated iodine being dependent on the amount of an acid (OH ions) in the sample added.

47. Determination of Persulphates (G. H. Mondolfo).

From 0.2 to 0.3 Gm. of the sample dissolved in 10 Cc. of water is transferred to a glass-stoppered bottle, 0.5 KI added, and the well-stoppered bottle is heated to 60°–80° C., during 10 minutes, in an air-bath. The contents are cooled, diluted with water, and the iodine titrated with $\frac{N}{10}$ thiosulphate V.S. in the presence of starch added near the end of the titration.

$$\underset{270.34}{K_2S_2O_8} \quad + \quad 2KI \quad = \quad \underset{2 \times 126.92}{2I} \quad + \quad 2K_2SO_4.$$
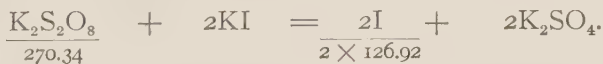
1 Cc. of $\frac{N}{10}$ thiosulphate corresponds to 0.013517 Gm. potassium persulphate.

48. Determination of Peroxides.

Also chromates, manganates, antimonic oxide (Sb_2O_5), arsenic pentoxide (As_2O_5), cerium oxide (CeO_2), etc.

Certain peroxides (of the heavy metals), and other oxidizing agents, liberate chlorine from hydrochloric acid. The liberated chlorine, distilled into KI solution, liberates an equivalent quantity of iodine which is titrated with standard thiosulphate.

Distillation Apparatus.—In its various forms the apparatus consists essentially of a small decomposition flask joined to a receiver by an adapter, the joints, as few as possible, being absolutely air tight.

The original, *Bunsen* form of the apparatus, Fig. 31, has a decomposition flask (d) of about 40 Cc. capacity, and this is joined to the adapter (a) by rubber tubing (c), though this kind of connection is now replaced by a ground glass joint. The free end of the bulbed adopter, which may also be straight, is narrowed into a fair sized capillary, and extends well into the receiver (b). The receiver is of the form of a bulbed retort and should hold about 250 Cc. During distillation the receiver is kept immersed in cold water.

In operation, the sample is placed in the decomposition flask together with the acid, and the chlorine gas generated is distilled into the receiver in which a solution of potassium iodide serves to absorb the chlorine.

In the *Fresenius* apparatus, Fig. 32, two absorption tubes (d and e in the figure) are used in place of the receiver of the Bunsen form. These tubes are joined to the decomposition flask (a) by a bent tube and the distillation is carried out as with the other appa-
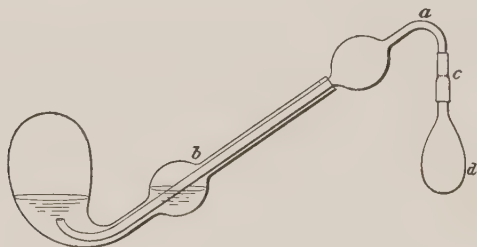
FIG. 31.   BUNSEN'S DISTILLATION APPARATUS.

ratus. The absorption tubes are placed in a jar of cold water to keep their contents (KI solution) at uniform temperature during distillation.

The *DeKoninck* apparatus, Fig. 33, has the decomposition flask (a) joined to a Volhard wash flask (b) which contains the KI solution, by an adapter (c). The Fresenius and DeKoninck forms do not allow the KI solution to be drawn over into the decomposition flask.

Another form of the apparatus which retains the KI solution in the receiver is that of *Topf,* in which the decomposition flask is replaced by a tubulated retort with a long stem.

All these forms of distillation apparatus may be replaced, with advantage, by the apparatus of Morgan and Cook (Analyst, 1908, 33, 117), which is constructed to permit the passing of a current of CO_2 through it during distillation.

Operation.—Volumetric solution employed: $\frac{N}{10}$ sodium thiosulphate.

Weigh accurately a suitable quantity of the sample (0.1 to 0.3

Gm.) into the dry decomposition flask, weighing by difference. Into the receiver place, of 5 per cent. KI, free from iodate, a sufficient quantity to fill the large bulb (Fig. 31) two thirds full. Add to the sample, in the decomposition flask, 5 to 20 Cc. of pure HCl,
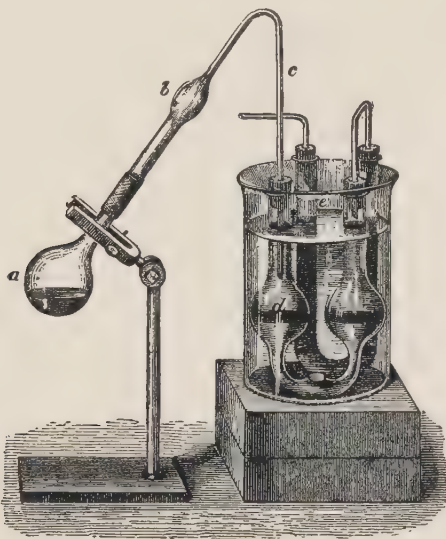
FIG. 32. FRESENIUS'S DISTILLATION APPARATUS.

free from chlorine, connect the apparatus at once and heat the flask with a small flame. Distill at gentle boiling until one half of the contents of the flask have been distilled over or until no further evolution of chlorine is observed. To discontinue the operation, disconnect the apparatus without removing the flame in order to prevent the KI solution from being drawn over into the decomposition flask. When the distillation is completed, pour the contents of the receiver into a large beaker, wash the adhering solution out with portions of water, then with some KI solution and titrate the free iodine with $\frac{N}{10}$ thiosulphate V.S. One drop of the V.S. should discharge the final light yellow color of the titrated liquid. Having carried out a check titration, calculate, from the results found, the percentage of the peroxide or other chlorine-liberating compound in the sample. The factor for any particular oxidizing agent determined by this method is derived from the equation representing the reactions involved, which may be typically represented by the following equations:

$$\underset{86.93}{MnO_2} \ + \ 4HCl \ = \ MnCl_2 \ + \ 2H_2O \ + \ \underset{2 \times 35.46}{2Cl.}$$

$$2Cl \ + \ 2KI \ = \ 2KCl \ + \ \underset{2 \times 126.92}{2I.}$$

$$2I \ + \ \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} \ = \ etc.$$
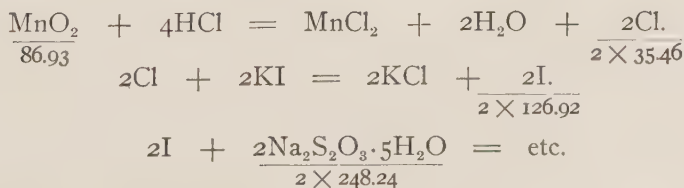
86.93 parts of MnO_2 liberate 2×35.46 parts of Cl which set free 2×126.92 parts of I, and these require 2×248.24 parts of sodium thiosulphate for reaction, so that
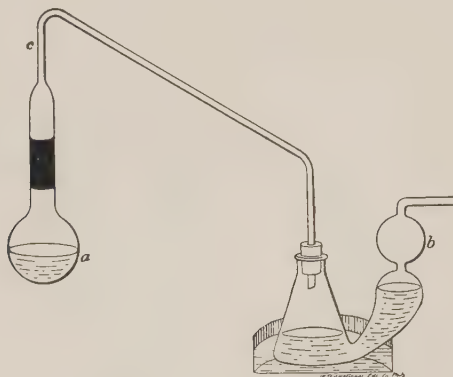
FIG. 33. DEKONINCK'S DISTILLATION APPARATUS.

$$\frac{86.93}{2} MnO_2 = 35.46 - Cl = 126.92 - I = 248.24 - Na_2S_2O_3 \cdot 5H_2O.$$
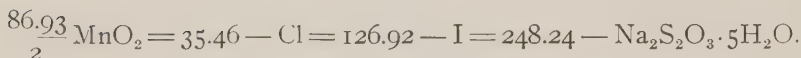
1 Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to $\frac{8.693}{2} = 4.346$ Gm. of MnO_2.

1 Cc. is the equivalent of 0.004346 Gm. of manganese dioxide.

Observations.—It need hardly be emphasized that any loss of chlorine means low results for the compound determined; hence the distilling apparatus must be absolutely airtight and the distillation carried out with care. The sources of loss are minimized by decreasing the number of connections. During distillation the receiver should be immersed in cold water. The liquid to be titrated will contain much HI, formed through the decomposition of the KI in solution by the HCl distilled into it. Since HI is decomposed by the oxygen of the air, iodine being set free, the entrance of air must be guarded against. The decomposition of HI may be minimized by filling the large bulb of the receiver with CO_2 before the KI solution is introduced; also by diluting the solution largely after distillation, and titrating immediately with the thiosulphate. Hydriodic acid is less readily decomposed in weak solutions (in ionized state) than in concentrated, the nonionized acid alone being attacked. Dilute solutions of samples must be concentrated before distillation.

Note.—Antimony, if in the form of Sb_2O_3, is oxidized by aqua regia or treated with HCl + Br or by H_2O_2 added to a concentrated solution made alkaline with KOH; the excess of the oxidizing agents must be removed by boiling. Precipitated Sb_2S_3 is dissolved in KOH and H_2O_2 added; the oxidation of its solution in KOH should be repeated. For CrO_3, $HClO_3$, MnO_2 and PbO_2 this method of treatment has been modified by V. Farsöe (Ztsch. anal. Chem.,

1907, 46, 308), in that $HBr(2KBr + H_2SO_4)$ is used and the Br liberated distilled into KI solution. For distillation, 1 to 2 Gm. of $KBr + 20$ Cc. $H_2SO_4 + 80$ Cc. of water are used and the distillation made in 15–20 minutes. As, at this concentration, HBr is not affected by H_2SO_4, weak solutions may be employed.

49. DETERMINATION OF SOLUBLE IODIDES.

(a) *By Distillation.*—The distillation is made after the method given for peroxides, the decomposition of the iodide being brought about by a ferric salt. The sample is weighed into the decomposition flask, an excess of ammonium ferric sulphate added, the solution acidified with diluted sulphuric acid and the liberated iodine distilled into KI solution for titration. From the volume of $\frac{N}{10}$ thiosulphate consumed, the percentage of the particular iodide is calculated. For equations and derivation of factors, see determination of ferric salts. Insoluble iodides are first changed into soluble by fusion with sodium carbonate or by treatment with $Zn + H_2SO_4$.

(b) *With Nitrous Acid (Method of Fresenius).*—The iodine of an iodide, of which only a small quantity should be treated, is set free by nitrous acid and titrated with standard thiosulphate V.S.

Volumetric solution employed: $\frac{N}{10}$ thiosulphate.

The solution of the sample contained in a special apparatus for decomposition (in place of which a well-stoppered separator may be used) is acidified with 10 per cent. sulphuric acid, few drops of " Nitrose "[1] added, and the liberated iodine dissolved out by shaking with several portions of pure CS_2 or $CHCl_3$. To the solution of the iodine in the volatile solvent one to two drops of $NaHCO_3$ solution are added and the liquid is titrated with $\frac{N}{10}$ thiosulphate V.S. One drop of the V.S. should, when finally added to the titrated liquid, discharge the violet, iodine color. Calculation of the percentage of an iodide present is readily made from the volume of $\frac{N}{10}$ thiosulphate consumed.

Notes.—This method is best suited for the determination of small quantities of iodides, in the presence of much of the other haloid salts, HCl and HBr not being decomposed by this treatment. It should be noted that iodine is not completely taken up by the volatile solvents so that exact results are obtained only by standardizing the thiosulphate with pure KI, the method of titration and the quantities and concentration of reagents used, being the same as in the determination.

To avoid distillation, iodides may be decomposed with a permanganate and the liberated iodine titrated. According to Rupp and Horn (Arch. der Pharm., 1906, 495), 0.25 to 0.5 Gm. of the sample is dissolved in 50 Cc. of water, and to the solution added, 25 Cc. of dilute sulphuric acid, 3 Gm. of oxalic acid, and then 10 Cc. of 1 per cent. of potassium permanganate. After the mixture has stood 3 hours, 1 Gm. of KI is added and the solution titrated with $\frac{N}{10}$ thiosulphate V.S.

[1] " Nitrose " is a solution of nitrosyl sulphuric acid in sulphuric acid. It may be prepared by passing nitrogen trioxide into strong sulphuric acid to saturation.

When the titration is carried out in this manner the presence of chlorides or bromides has no effect on the results.   From the volume of $\frac{N}{10}$ thiosulphate consumed, the percentage of iodide in sample is calculated.   For reactions, see standardization of permanganate by thiosulphate, p. 99.

50. DETERMINATION OF FORMALDEHYDE (IN SOLUTION OF F—.).

Formaldehyde is oxidized in alkaline solution by an excess of standard iodine V.S. to formic acid and the unconsumed iodine is titrated with $\frac{N}{10}$ thiosulphate.

Volumetric solutions employed: $\frac{N}{10}$ iodine and $\frac{N}{10}$ thiosulphate.

To 50 Cc. of the $\frac{N}{10}$ iodine, in a titration flask, add 5 Cc. of a 1–30 solution of the sample (dilute 10 Gm. to measure exactly 300 Cc.), or as much of a weaker solution as will contain 0.15 Gm. of formaldehyde.   Drop in, at once, 10 per cent. NaOH solution until alkaline reaction is produced in the liquid, which becomes light yellow in color, and set aside for 10 minutes.   Acidify with dilute acetic acid and titrate with the $\frac{N}{10}$ thiosulphate V.S.   The number of Cc. of this V.S., subtracted from 50, gives the volume of $\frac{N}{10}$ iodine consumed by the formaldehyde and from this the percentage of it in the sample is calculated.   The reaction of formaldehyde with iodine is represented:

$$\underset{30.02}{\text{HCHO}} + \underset{2 \times 126.92}{2\text{I}} + \text{H}_2\text{O} = 2\text{HI} + \text{HCOOH.}$$
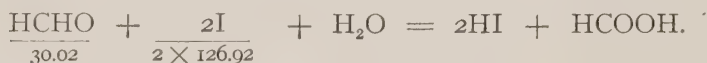
1 Lt. of $\frac{N}{10}$ iodine contains 12.692 Gm., and corresponds to 1.501 Gm. of HCOH.

1 Cc. is, therefore, the equivalent of 0.001501 Gm. of formaldehyde.

The hypoiodide solution is decomposed by HCl.   Reliable results are obtained only when comparatively pure solutions of formaldehyde are treated.

51. DETERMINATION OF FORMIC ACID (RUPP).

The acid is oxidized by an excess of standard hypobromite and the excess of this reagent determined iodometrically.

Volumetric solutions employed: Standard hypobromite (see 52) and $\frac{N}{10}$ thiosulphate.

A suitable quantity of the acid is oxidized by an excess of the standard hypobromite in a glass-stoppered cylinder, the method given for the determination of ammonium compounds being followed.   The unconsumed hypobromite is found by titration, with $\frac{N}{10}$ thiosulphate, of the iodine it liberates from an iodide.

Reactions:

$$\underset{46.02}{\text{HCOOH}} + \text{NaOBr} = \text{H}_2\text{O} + \text{CO}_2 + \text{NaBr.}$$

$$\text{NaOBr} + 2\text{HI} = \underset{2 \times 126.92}{2\text{I}} + 2\text{NaBr} + \text{H}_2\text{O.}$$

$$2I + \underline{2Na_2S_2O_3 \cdot 5H_2O} = etc.$$
$$2 \times 248.24$$
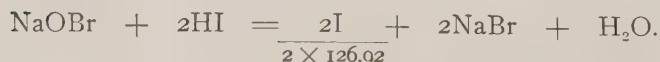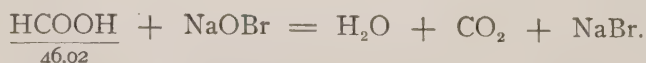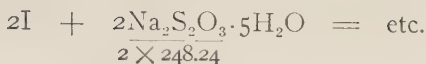
46.02 parts of HCOOH correspond to 2×248.24 parts of $Na_2S_2O_3 \cdot 5H_2O$.

1 Cc. of $\frac{N}{10}$ thiosulphate therefore corresponds to 0.002301 Gm. of formic acid.

To calculate percentage of the acid assayed by this method, the Cc. of $\frac{N}{10}$ thiosulphate consumed in titration are deducted from the Cc. $\frac{N}{10}$ thiosulphate required to titrate an exactly equal volume of the hypobromite, treated as in the determination, and the difference in volumes which corresponds to the acid present, is used for calculation of its percentage.

$$\frac{N. Cc. \frac{N}{10} \text{ thio. corr. to acid} \times 0.002301 \times 100}{\text{Weight of sample}} = \text{per cent. of formic acid.}$$

52. Determination of Ammonium Compounds (Rupp and Roessler).[1]

Ammonium compounds are decomposed by an excess of standard alkali hypobromite, the excess of which is titrated iodometrically.

Volumetric solutions employed: $\frac{N}{10}$ thiosulphate and standard hypobromite. To prepare the latter, dissolve 19 Gm. of NaOH in 500 Cc. of water, add slowly 17 Gm. of bromine, mixing well, and keep the solution well stoppered. The exact strength of the solution is found, at the time of use, by titration with $\frac{N}{10}$ thiosulphate V.S.

Measure accurately a suitable volume of the hypobromite (5 to 6 Cc.) into a glass-stoppered cylinder, add 75 Cc. of recently boiled and cooled water and add the solution of the sample. This should contain a definite, known amount (0.2 Gm.) of the sample and should measure about 10 Cc. Let stand 5 to 10 minutes, add 5 Cc. of water, acidify with dilute HCl, add 2 Gm. of KI, let stand 2 minutes, and titrate with the $\frac{N}{10}$ thiosulphate V.S. One drop of the V.S. should discharge the final yellow color of the titrated liquid. Having treated an exactly equal volume of the hypobromite precisely as in the determination, and then titrated the liberated iodine with the $\frac{N}{10}$ thiosulphate, subtract from the volume of this the Cc. of $\frac{N}{10}$ thiosulphate consumed in the determination; the difference in volumes of the $\frac{N}{10}$ thiosulphate will correspond to the hypobromite consumed by the ammonium compound present. From the volume of the $\frac{N}{10}$ thiosulphate which corresponds to the hypobromite consumed by the ammonium salt, the percentage of the salt in sample is calculated. Equations:

$$\underline{2NH_3} + 3NaOBr = 2N + 3H_2O + 3NaBr.$$
$$2 \times 17.04$$

$$NaOBr + 2HI = \underline{2I} + NaBr + H_2O.$$
$$2 \times 126.92$$

[1] Arch. der Pharm., 1905, 104–14.

$$2I \quad + \quad \underset{2 \times 248.24}{2Na_2S_2O_3 \cdot 5H_2O} \quad = \quad etc.$$
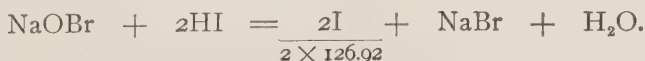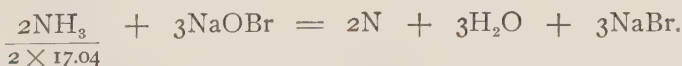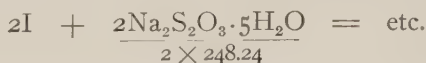
$\dfrac{17.04}{3}$ parts of NH_3 correspond to 248.24 parts of thiosulphate.

1 Lt. of $\frac{N}{10}$ thiosulphate contains 24.824 Gm., and corresponds to 0.568 Gm. of NH_3.

1 Cc. of the V.S. is the equivalent of 0.000568 Gm. of ammonia.

The excess of the hypobromite should be about one third to one half, and the ammonium salt must be added to the hypobromite. Potassium iodide is to be added only after the solution has been acidified. For determination of free ammonia, the solution of the sample should be largely diluted with ammonia-free water and, after decomposition, the HCl added drop by drop until the liquid becomes yellow.

As a check for the end-point, the titration should be completed with starch as indicator, in which case the discharged blue color must not reappear within one minute. The strength of solutions of ammonium salts best suited for treatment should be about 2 per cent., of ammonium hydroxide, 0.5 per cent.

53. DETERMINATION OF COPPER (JAMIESON, LEVY AND WELLS).[1]

Cuprous thiocyanate is oxidized to sulphate by a standard solution of potassium iodate.

Volumetric solution employed: Empirical potassium iodate. This is prepared by dissolving the exact amount (10.701 Gm.) of the pure reagent in distilled water to 1000 Cc. If the salt is not absolutely pure, a stronger than $\frac{N}{20}$ of formula-weight solution is made and standardized with pure Cu, the method of determination being followed.

Dissolve a suitable quantity of the copper salt in water or employ the neutral solution of copper obtained in separation of Cu from other metals, add 10 to 20 Cc. of 6 per cent. sulphurous acid, heat to boiling and precipitate the Cu as CuSCN with an excess of 10 per cent. ammonium thiocyanate. Let stand 10 minutes, filter and wash the precipitate until free from thiocyanate. Transfer the washed precipitate, with the filter to the precipitation flask, add 5 Cc. of chloroform, 30 Cc. of HCl, and 20 Cc. of water, mix well, and titrate with the standard KIO_3. The V.S. should be added in 0.5 Cc. portions and the flask closed and shaken after each addition. When the chloroformic layer has taken on a violet color, which becomes paler on further addition of the V.S., the titration should progress drop by drop until the violet color, which then disappears sharply, is discharged by one drop of the V.S. From the volume of the standard KIO_3 consumed, the percentage of the Cu present is calculated. The factor for Cu, with standard KIO_3 V.S., is derived from the equation:

[1] J. Am. Ch. Soc., 1908, 5, 760.

$$\frac{4CuSCN}{\underset{4\times 63.57\,(Cu)}{4\times 121.65}} + \underset{7\times 214.02}{7KIO_3} + 14HCl$$

$$=4CuSO_4 + 7ICl + 7KCl + 4HCN + 5H_2O.$$
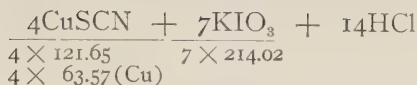
7×214.02 parts KIO_3 react with 4×63.57 parts of Cu in form of CuSCN.

If 1 Lt. of $\frac{N}{20}$ (of formula-weight) KIO_3 contains 10.701 Gm. and corresponds to 1.817 Gm. copper,

1 Cc., therefore, corresponds to 0.001817 Gm. of metallic copper.

Note.—Presence of organic matters, such as filter paper, alcohol, acetic or formic acid does not interfere with the titration. Heavy metals (Pb, Sb and Ag) must not be present. They are removed by evaporation of the solution with sulphuric acid to dryness, heating until SO_3 fumes are given off; the residue is then taken up with water or, if Ag is present, with a few drops of dilute HCl, filtered, the precipitate washed and the filtrate and washings, after neutralization with ammonium hydroxide, are treated as given above.

This method is applicable to other thiocyanates.

Standard potassium iodate V.S. has been recommended for the determination of many substances by L. W. Andrews (J. A. Ch. Soc., 1903, 25, 756), who pointed out the stability of ICl in the presence of a large excess of an acid. Chromates, chlorides, iodides, iodine, arsenic and antimony and ferrous compounds may be determined by it; the last three in the presence of Cu and ferric compounds.

54. Determination of Bromate (Gooch and Blake).

Bromate is caused to oxidize arsenous acid used in excess, the excess of the acid is titrated with standard iodine V.S.

Volumetric solutions employed: $\frac{N}{10}$ arsenous acid and $\frac{N}{10}$ iodine.

To a measured volume of $\frac{N}{10}$ arsenous acid V.S., contained in a flask, is added a weighed quantity of the sample, or a definite volume of a solution of known strength, then 3 to 10 Cc. of sulphuric acid (1–1) are introduced, and the mixture placed on water-bath for 30 minutes or boiled 10 to 15 minutes. After such time the free acid is neutralized with an alkali, $KHCO_3$ added in excess, and the solution titrated with $\frac{N}{10}$ iodine V.S., using starch solution as indicator. One drop of the V.S. should finally produce a distinct blue color. From the volume of $\frac{N}{10}$ arsenous acid, oxidized by the bromate, the percentage of it, or of bromic acid in the sample, is calculated. To represent the reactions:

$$\underset{3\times 126.03}{3H_3AsO_3} + \underset{128.93}{HBrO_3} = 3H_3AsO_4 + HBr.$$

$$3H_3AsO_3 + \underset{6\times 126.92}{6I} + 3H_2O = 3H_3AsO_4 + 6HI.$$
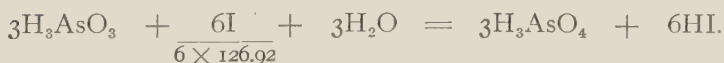
128.93 parts of bromic acid react with 3×126.03 parts of arsenous acid. $2H_3AsO_3 = As_2O_3.$

1 Lt. of $\frac{N}{10}$ As$_2$O$_3$ contains 4.95 Gm., and corresponds to 21.49 Gm. HBrO$_3$.

1 Cc. of the V.S. corresponds to 0.002149 Gm. of bromic acid, or 0.002784 Gm. of potassium bromate.

Boiling from 10–15 minutes is found to be the most favorable; at room temperature 30–120 minutes are required. Chlorate does not react under these conditions.

55. DETERMINATION OF CHROMIUM AS CHROMATE (IN STEEL).

Volumetric solutions required: $\frac{N}{10}$ thiosulphate and $\frac{N}{10}$ iodine.

Indicator: Starch solution.

The chromium is oxidized to a chromate which is then titrated.

Of the steel turnings, 1.667 Gm. or double that quantity is weighed into a beaker, 25 to 30 Cc. of HCl (1.124) added for solution and the ferrous salt oxidized by boiling with 25 Cc. of 8 per cent. solution of KClO$_3$. When free chlorine has been removed by heating, the solution is neutralized with 40 per cent. solution of sodium carbonate, transferred to an erlenmeyer flask and the chromium oxidized with an excess (10 to 20 Cc.) of 4 per cent. permanganate solution, boiling about 15 minutes. The excess of permanganate is removed by the addition of a little alcohol, and boiling 10 minutes longer. The solution is then made up to exactly 500 Cc., with distilled water, shaken frequently, and filtered through a dry filter. The filtrate is titrated in 50 Cc. portions, each portion being acidified with dilute HCl, 0.5 Gm. of KI, free from iodate, added and, after shaking the iodine set free is titrated with $\frac{N}{10}$ thiosulphate V.S. Residual titration being preferred the thiosulphate V.S. is added in excess, a little starch solution added and $\frac{N}{10}$ iodine V.S. run in carefully until a blue color is produced. From the volume of $\frac{N}{10}$ thiosulphate V.S., which corresponds to the chromate, the percentage of chromium is calculated. With 1.667 Gm. the $\frac{N}{10}$ thiosulphate $\times$ 0.17362 $\times$ 6 $=$ per cent. of chromium.

56. DETERMINATION OF CARBON DISULPHIDE.

Volumetric solutions required: $\frac{N}{10}$ thiosulphate and standard copper acetate. A nearly $\frac{N}{10}$ V.S. is prepared and its exact strength established by titration with $\frac{N}{10}$ thiosulphate V.S.

Indicator: Starch solution.

From 0.1 to 0.2 Gm. of the sample to be titrated are dissolved in 60–70 Cc. of pure benzene, in a glass-stoppered flask or bottle, an alcoholic solution of KOH added and the contents mixed by shaking during one half hour. The mixture is then transferred to a separator and shaken out with 30–40 Cc. of cold water, and 1 Cc. alcoholic KOH, repeatedly, until all potassium xanthate is extracted. The aqueous solution is diluted to measure 500 Cc. and 200 portions employed for precipitation. The portions are acidified with acetic acid, an excess of standard copper acetate solution added and the mixture stirred 10–15 minutes. After that, the precipitate of copper xanthate is filtered off, washed with 10–15 Cc. of cold water, 3 to 4 times, or until all copper acetate is washed out. The filtrate

and washings are combined, 3 Gm. of powdered KI added, allowed to stand 3 minutes, and the liberated iodine titrated with $\frac{N}{10}$ thiosulphate V.S. and the starch indicator. From the volume of standard Cu acetate V.S consumed by the xanthate, the quantity of CS_2 yielding it, and the percentage of the disulphide in sample, are calculated.

The ratio of $CuO:CS_2$ was found, by Harding and Doran (J. A. Chem. Soc., 1907, 29, 1476), to be 1:1.927.

57. IODINE ABSORPTION NUMBER OF FATS AND OILS (HUEBEL OR HANUS NUMBER).

Oils and fats, among other substances, possess the property of taking up iodine, when brought in contact with it, in solution. Under fixed conditions the quantity of iodine thus absorbed is definite for the individual fats; as this varies with the fats it constitutes, when properly determined, an evidence of much value in the examination of these substances for purity and identity. The percentage of iodine absorbed by a given fat under definite conditions constitutes the number.

Reagents:

Standard Iodine Solution.

An alcoholic solution of iodine containing mercuric chloride and known as Huebel's iodine solution, is made by dissolving 26 Gm. of sublimed iodine in 500 Cc. of 95 per cent. alcohol and mixing the solution with a clear solution of 30 Gm. of $HgCl_2$ in 500 Cc. of alcohol of the same strength. The mixture should be allowed to stand a day before it is employed for determination.

Acetic acid solution of iodine and bromine, the Hanus's iodine solution is prepared by dissolving 13.2 Gm. of sublimed iodine in 1 Lt. of glacial acetic acid, heating, if need be; to the cold solution are added 3 Cc. of pure bromine.

Both solutions are to be kept in glass-stoppered bottles They are standardized at the time of their employment for the determination of the number.

Potassium Iodide Solution, 20 per cent.

Tenth-N Sodium Thiosulphate V.S.

The quantity of the sample to be treated should be so adjusted as to consume from 20 to 40 Cc. of the standard iodine solution. Of fats, 0.5 Gm., non-drying oils, 0.25 Gm., and of drying oils, 0.1 to 0.2 Gm., will be found a suitable quantity.

The sample is weighed, preferably by difference, into a flask or bottle, dissolved in 10 Cc. of chloroform and 30 to 50 Cc. of the iodine solution, carefully measured, are run in from a burette; the excess of iodine should be at least as much as the iodine consumed. With Huebl's solution the mixture is allowed to stand 4 hours in a dark place in a closed bottle; with the Hanus's solution it should be shaken during one half hour. Into another flask an equal vol-

ume of the iodine solution, used for the fat, is accurately measured, 10 Cc. of $CHCl_3$ added, and the contents treated precisely as in the determination.

After standing the required length of time the unconsumed iodine is determined by titration. Should no iodine be found left unconsumed, 20 to 30 Cc. more of the iodine solution should be added and the treatment repeated. The titration of the iodine is to be made in the presence of KI, 20 Cc. of the solution of which, together with 50 Cc. of water, are added and the $\frac{N}{10}$ thiosulphate V.S. run in with a thorough agitation of the titrated liquid until the final yellow color of iodine is just discharged by one drop of the V.S. Should the liquid be colored and the end-reaction interfered with, 0.5 Cc. of starch solution may be added when the end of the titration is approached, and the V.S. run in until the blue color is just discharged by one drop of it, while the titrated liquid is kept constantly agitated. The chloroform present may also be made to serve as an indicator. (See standardization of $\frac{N}{10}$ thiosulphate by $K_2Cr_2O_7$.) The iodine solution (without fat) is titrated in the same manner. The volume of $\frac{N}{10}$ thiosulphate V.S. consumed by the iodine solution in the blank, less the Cc. of the V.S. required for the unconsumed iodine, gives Cc. of $\frac{N}{10}$ thiosulphate V.S. which correspond to the iodine absorbed by the fat. Since 1 Cc. of $\frac{N}{10}$ thiosulphate V.S. is the equivalent of 0.012692 Gm. of iodine, the percentage of the absorbed iodine is calculated:

$$\frac{\text{Cc. of } \frac{N}{10} \text{ thio. corr. to I absorbed} \times 0.012692 \times 100}{\text{Weight of fat taken}} = \text{I absorption No.}$$

TABLES OF EQUIVALENTS (*factors*).

1. TENTH-NORMAL PERMANGANATE V.S.

1 Cc. of $\frac{N}{10}$ potassium permanganate V.S. contains 0.0031606 Gm. of $K_2Mn_2O_8$ and is the equivalent of:

	Gramme.
Ammonium persulphate $(NH_4)_2S_2O_8$	0.008112
Calcium, Ca	0.0020045
Calcium oxide, CaO	0.0028045
Calcium hypophosphite, $Ca(PH_2O_2)_2$	0.002126
Ferric hypophosphite, $Fe(PH_2O_2)_3$	0.0020909
Ferrous ammonium sulphate, $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	0.039221
Ferrous carbonate, $FeCO_3$	0.011585
Ferrous chloride, $FeCl_2$	0.012677
Ferrous sulphate, anhydrous, $FeSO_4$	0.015192
Ferrous sulphate, crystalline, $FeSO_4 \cdot 7H_2O$	0.027806
Ferrous sulphate, dried, $2FeSO_4 \cdot 3H_2O$	0.017895
Formaldehyde, HCHO	0.001501
Formic acid, HCOOH	0.0013806
Hydrogen dioxide, H_2O_2	0.001701
Hydrogen sulphide, H_2S	0.0017045
Hypophosphorous acid, HPH_2O_2	0.00165075
Iron, Fe	0.005585

Gramme.

Lead, Pb (as oxalate) 0.010355
Lead, Pb (as nitrate in alkaline solution)................ 0.012426
Lead acetate, $Pb(C_2H_3O_2)_2 \cdot 3H_2O$......................... 0.018961
Lead subacetate, $Pb_2O(C_2H_3O_2)_2$ 0.013706

Manganese hypophosphite, $Mn(PH_2O_2)_2 \cdot H_2O$ 0.0025374
Manganese dioxide, MnO_2 .... 0.004346
Oxalic acid, $H_2C_2O_4 \cdot 2H_2O$ 0.006303
Oxygen, O 0.000800

Potassium chlorate, $KClO_3$ 0.0020425
Potassium hypophosphite, KPH_2O_2 .... 0.00260425
Potassium ferrocyanide, $K_4FeCN_6 \cdot 3H_2O$ 0.042237
Potassium ferricyanide, K_3FeCN_6 .... 0.032921
Potassium nitrate, KNO_3 .... 0.0033703
Potassium nitrite, KNO_2 .... 0.004258
Potassium percarbonate, $K_2C_2O_6 \cdot H_2O$ 0.0108II
Potassium persulphate, $K_2S_2O_8$ 0.013517
Potassium sulphide, K_2S 0.0055135

Sodium chlorate, $NaClO_3$ 0.017743
Sodium dioxide, Na_2O_2 .... 0.00390
Sodium hypophosphite, $NaPH_2O_2 \cdot H_2O$ 0.002651
Sodium nitrate, $NaNO_3$ 0.002834
Sodium nitrite, $NaNO_2$ 0.0034505
Sodium perborate, $NaBO_3 \cdot 4H_2O$ 0.007705
Sodium persulphate, $Na_2S_2O_8$ 0.0119110

2. Tenth-Normal Iodine V.S.

1 Cc. of $\frac{N}{10}$ iodine V.S. contains 0.012692 Gm. of iodine and is the equivalent of:

Gramme.

Ammonia, NH_3 .... 0.000568
Antimony, Sb 0.00601
Antimony and potassium tartrate, $2K(SbO)C_4H_4O_6.H_2O$.. 0.016618
Antimony oxide, Sb_2O_3 .... 0.00721
Arsenic, As 0.00375
Arsenic trioxide (arsenous acid), As_2O_3 .... 0.00495
Arsenous iodide, AsI_3 .... 0.022788
Formaldehyde, HCHO 0.001501
Formic acid, HCOOH 0.002301
Hydrogen sulphide, H_2S 0.0017045
Iron, Fe 0.0027925

Mercury, Hg 0.0100
Mercuric chloride, $HgCl_2$ 0.013546
Mercuric cyanide, $HgCN_2$ 0.012604
Mercurous chloride, Hg_2Cl_2 (titrated) 0.023546

Potassium sulphite, crystalline, $K_2SO_3 \cdot 2H_2O$ 0.0097155
Potassium bisulphite, $KHSO_3$ 0.00601
Sodium bisulphite, $NaHSO_3$ 0.005204
Sodium sulphite, $Na_2SO_3 \cdot 7H_2O$ 0.01261
Sodium thiosulphate, $Na_2S_2O_3 \cdot 5H_2O$ 0.024824
Sulphurous acid, H_2SO_3 .... 0.0041045
Sulphur dioxide (sulphurous anhydride), SO_2 .... 0.0032035

3. Tenth-Normal Thiosulphate V.S.

1 Cc. of $\frac{N}{10}$ sodium thiosulphate V.S. contains 0.024824 Gm. of $Na_2S_2O_3 \cdot 5H_2O$ and is the equivalent of:

12

Gramme.

Bromine, Br	0.007992
Chlorine, Cl	0.003546
Chromium trioxide, CrO_3	0.00387
Copper, Cu	0.006357
Copper sulphate, $CuSO_4 \cdot 5H_2O$	0.024974
Hydrogen dioxide, H_2O_2	0.001701
Hypochlorous acid, HClO	0.005247
Iodine, I	0.012692
Iron, Fe	0.005585
Magnesium, Mg	0.001216
Magnesium oxide, MgO	0.002016
Manganese dioxide, MnO_2	0.004346
Potassium bromate, $KBrO_3$	0.002784
Potassium chlorate, $KClO_3$	0.002043
Potassium iodate, KIO_3	0.003567
Potassium persulphate, $K_2S_2O_8$	0.013517
Sodium chlorate, $NaClO_3$	0.001774

CHAPTER IV.

Determinations by Precipitation.

In this division are included those methods of volumetric determination of substances in which precipitation, that is, separation of solid substances from solution, takes place. In most cases the substance to be determined is precipitated by means of a volumetric solution of a suitable reagent added until the reaction is completed. The simplest method of ascertaining, through end-reaction, the completion of precipitation reactions is to add the precipitant until no further precipitation takes place and this is often practiced; but since, in most cases, the resulting mixture remains cloudy—the suspended particles of the precipitate not depositing readily—this method is not found generally applicable.

As in the other methods of volumetric analysis, the reagents employed are standard solutions, chiefly tenth-normal or weaker. The indicators used are not many and are mostly solutions of salts. They are, as a rule, added to the titrated liquid except when the substances themselves would react with them; in such cases the "drop end-point" method must be resorted to. For this a drop of the titrated liquid is removed and brought into admixture with a drop of the indicator, on a white surface, to obtain the end-reaction which is indicated by the production of a distinct color or the formation of a precipitate. When applied negatively, the nonappearance of a given color or the nonformation of a precipitate are the end-point indications.

In order that any substance may be accurately determined by precipitation, the reaction utilized must, of necessity, be quantitative, and in addition, there must be a definite end-reaction to indicate the completion of the precipitation. It is chiefly on account of the difficulty to satisfy the latter requirement that precipitation reactions, so common in gravimetric analysis, are not more available for volumetric methods.

Precipitation may be due to numerous causes; that caused by chemical reaction alone is here considered. The empirical facts— that any substance, formed from other substances in such solvent in which the new substance is insoluble, separates as a precipitate— still hold. In view of the ionic state of substances in solution the causes and operations of precipitation have become better understood and many, formerly unexplainable manifestations are being explained. The newer views hold, that, when a substance has separated from a solution in solid form, the solution remains saturated with it and that on that account, precipitation takes place only under conditions of supersaturation. The quantity of the precipitate which remains in solution after precipitation depends mainly on its solubility or insolubility, the temperature of the solution and, to some

extent, on the pressure upon it and on the quantities of other substances present in the solution.

The solubility of a precipitate in quantitative determinations should be as small as possible. Where only a very small quantity of the precipitate remains dissolved, its ionization is regarded to be complete. The product of the concentrations, in a saturated solution, of the component ions, denoted as the "solubility product" (Ostwald) has a constant value for the same substance. When this value of the solubility product of any substance in solution has been reached, the solution is saturated with the substance; when it is exceeded, precipitation takes place and, if the value is not reached, the solution acts as a solvent and will take up some more of the substance in question. Thus, when two electrolytes are brought together in solution and the solubility product of certain ions is thus exceeded, precipitation ensues and ends only when the excess of the compound formed has deposited, and thus the solubility product of the particular substance reached. So that any cause which will produce oversaturation will increase the amount of the separated precipitate.

It has long been known that precipitation is more complete in many instances when an excess of either of the reacting substances is used. This is ascribed to be due to the influence which the presence of an ion in common with an ion of the compound in solution exerts. In view of the ionized condition of the remaining precipitate, the addition of such an ion increases its concentration and its solubility product is exceeded. The solution being already saturated, that is, the solubility product reached, precipitation must result, more of the precipitate separating. The amount of the precipitate thus separated is proportional to the quantity of the reacting substance used in excess.

This precipitation, ending as it does only when an excess of the reagent has been added, is practiced in gravimetric analyses but can not be carried out to any such point in the volumetric methods. The end-reaction in titration is indicated when only a minute excess of a reagent has been added, or, in other words, the titration is ended before the precipitation is as complete as it could be made. It is therefore of the utmost importance to carry out titrations of this kind under as nearly as possible similar conditions with those obtaining in standardization of the volumetric solutions employed.

When a sample is found to contain other substances which would modify the involved reaction or interfere with the precipitation, such substances must be removed or rendered harmless before titration. When their removal is found impracticable and the quantity of the interfering substances is known, it is sometimes of advantage to add them to the blank in the proportion in which they are contained in the sample.

VOLUMETRIC SOLUTIONS.

Tenth-normal Silver Nitrate V.S.

1000 Cc. contain 16.989 Gm. of AgNO₃.

This is usually directed to be prepared from pure $AgNO_3$, dried at 120° C., for 10 minutes, of which the required quantity, 16.99 Gm , is dissolved in distilled water to measure, at standard temperature, exactly 1000 Cc (or 17 Gm., dissolved to measure 1000.60 Cc.). For exact strength, this solution is best prepared from pure metallic silver.

Preparation of Pure Silver.—A suitable quantity of silver nitrate (20 Gm.) is dissolved in water and the silver precipitated with an excess of a clear solution of sodium chloride. After thorough mixing, the silver chloride is filtered off, washed by decantation several times with water, transferred to a clean porcelain dish, an excess of dilute alkali added, the mixture heated to boiling, and grape sugar gradually added in small portions When the reduction of the AgCl to Ag is complete—a portion of the gray precipitate should dissolve clear in pure HNO_3—the supernatant liquid is decanted, the precipitate washed with hot water and dried. The dry powder is then melted on a lime support in a blast flame, the melted metal on cooling boiled in dilute sulphuric acid and, after drying, heated to redness. The pure metal thus obtained is kept in a well-closed bottle. To prepare the $\frac{N}{10}$ V.S. the required quantity is accurately weighed and dissolved in nitric acid.

To prepare the tenth-normal $AgNO_3$ V.S., 10.788 Gm of the pure silver are weighed into an erlenmeyer flask, the metal dissolved in a small quantity of pure HNO_3, the flask being kept covered with a small funnel. The solution is boiled to remove all nitrous acid, any red fumes removed by a current of air. The funnel and flask are then well washed with water, the solution is diluted to measure, at standard temperature, exactly 1000 Cc. and placed in a clean, dark-colored bottle in which it is kept in a cool place protected from dust. The solution thus prepared contains free nitric acid (to which there is no objection when used for Volhard titration) and therefore has acid reaction; to obtain, by this method, a solution free from acid, the solution of silver in nitric acid must be evaporated to dryness and the residue dissolved. When any uncertainty exists as to the purity of the silver nitrate to be used for V.S., a stronger than $\frac{N}{10}$ solution of the salt is made and its strength adjusted with $\frac{N}{10}$ NaCl V.S.

Silver nitrate V.S. may be standardized gravimetrically, that is by precipitation of the silver in a given volume of the solution with an excess of NaCl, washing, drying and weighing the AgCl obtained. This is hardly ever necessary. As to the utility of gravimetric standardization of volumetric solutions, see p. 51.

Tenth-normal Sodium Chloride V.S.

1000 Cc contain 5.846 Gm. of NaCl.

Weigh very accurately 5.846 Gm. of pure, dry, sodium chloride, dissolve in distilled water and dilute the solution to measure, at standard temperature, exactly 1 Lt. Keep the solution in a clean, glass-stoppered bottle

Preparation of Pure Sodium Chloride.—Prepare a saturated solution of 10 to 15 Gm. of crystalline sodium chloride, filter the solution, pass HCl gas through it, keeping the solution cold. Filter through a hardened filter paper, wash several times with small portions of concentrated, pure HCl, drain the crystals well and dry on water-bath. When dry, powder the product fine in an agate mortar and heat in platinum to dull redness. After cooling in a desiccator, transfer it to a clean, dry bottle for keeping, or weigh and dissolve the required quantity for $\frac{N}{10}$ V.S. Tenth-normal NaCl V.S. should correspond, volume for volume, with the $\frac{N}{10}$ AgNO$_3$. Empirical NaCl V.S. may be standardized by titration with $\frac{N}{10}$ AgNO$_3$ according to Mohr or Volhard method.

Tenth-normal Thiocyanate V.S. (KSCN or NH$_4$SCN.)
VOLHARD SOLUTION.

1000 Cc. of the solution contain: $\begin{cases} \text{9.718 Gm. of KSCN or} \\ \text{7.613 Gm. of NH}_4\text{SCN.} \end{cases}$

Prepare a stronger than $\frac{N}{10}$ solution of the pure salt by dissolving 10 Gm. of the potassium salt or 8 Gm. of the ammonium compound in 1000 Cc. of distilled water and standardize the solution by titration.

Standardization with $\frac{N}{10}$ Silver Nitrate V.S.—Into a titration flask measure exactly 20 Cc. of $\frac{N}{10}$ AgNO$_3$ V.S., add 1 Cc. of ammonium ferric sulphate solution, 5 Cc. of diluted nitric acid (10 per cent., and free from nitrous), dilute to 100 Cc and titrate with the stronger thiocyanate solution. Allow this solution to run from a burette into that of silver nitrate, in small portions, mixing well after each addition and, when the silver in solution has been nearly all precipitated, that is when the reddish color produced by the added solution begins to disappear slowly on mixing, reduce the flow to drops. Continue to add drop by drop, mixing well by shaking so that finally one drop of the thiocyanate solution produces a distinct, permanent reddish color. Read the burette carefully and, having confirmed the correctness of the reading by another titration, dilute the thiocyanate solution to the tenth-normal strength. Since 20 Cc. of $\frac{N}{10}$ AgNO$_3$ are titrated, the difference between the Cc. of the thiocyanate used and 20 represents the volume of water to be added to change the indicated number of Cc. of the stronger thiocyanate to the $\frac{N}{10}$ value. Thus, if 18.4 Cc. of the stronger thiocyanate were consumed, with 20 Cc. of $\frac{N}{10}$ AgNO$_3$, these and every 18.4 Cc of the solution are to be diluted, at standard temperature, to exactly 20 Cc., and therefore 1.6 Cc. of distilled water must be added to them. After dilution the correctness of the standard

solution should be confirmed by another titration in which 40 Cc. of $\frac{N}{10}$ AgNO$_3$ V.S. should be used and, if it be found necessary, another adjustment made. Equations:

$$\underset{16.989}{AgNO_3} + \underset{97.18}{KSCN} = AgSCN + KNO_3.$$

$$(NH_4)_2Fe_2(SO_4)_3 + 6KSCN$$
$$= \underset{\text{red colored.}}{2Fe(SCN)_3} + 3K_2SO_4 + (NH_4)_2SO_4.$$
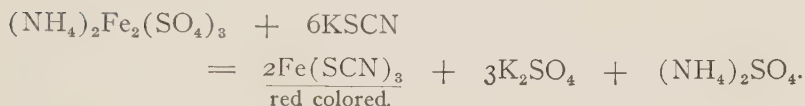
Second equation represents the formation of the red-colored ferric thiocyanate which occurs when all the silver has combined with the thiocyanate added.

Observation.—When a solution of thiocyanate is added to silver nitrate AgSCN separates as a white precipitate insoluble in diluted nitric acid; this reaction alone takes place as long as any silver is in the solution. When all the silver has reacted, the thiocyanate added then reacts with the ferric salt, producing with it a soluble ferric thiocyanate of red color. Thus a minute excess of thiocyanate added is at once indicated by the appearance of a reddish color which should not disappear on mixing. With a large quantity of AgSCN formed in this manner the delicacy of the end-reaction is impaired; under those conditions the AgSCN should be removed by filtration just before the permanent red color is obtained and the filtrate and washings titrated to a permanent reddish color.

EMPIRICAL POTASSIUM CYANIDE V.S.

KCN = 65.11.

The solution is best prepared and standardized when required. For a nearly $\frac{N}{10}$ solution approximately 7 Gm. of pure potassium cyanide are dissolved in distilled water to measure 1000 Cc. The solution is used mainly for determination of copper and should, for this purpose, be standardized with pure copper (electrolytic). When employed for determination of formaldehyde its standardization is best made with $\frac{N}{10}$ AgNO$_3$ V.S. Directions for these operations will be found described under the respective determinations.

EMPIRICAL POTASSIUM FERROCYANIDE V.S.

K$_4$FeCN$_6$·3H$_2$O = 422.37.

An approximately $\frac{N}{10}$ V.S. is prepared by dissolving 43 Gm. of the pure, crystalline salt, in water, to measure 1000 Cc. The solution is standardized, when employed for zinc determinations, with pure Zn or ZnO. The metal or the oxide is dissolved in HCl at the time of the determination, and with this solution that of the ferrocyanide is standardized.

STANDARDIZATION WITH ZINC OR ZINC OXIDE.

Preparation of Solution.—Weigh accurately 10 Gm. of C.P. zinc or 12.4465 Gm. of ZnO (freshly ignited and cooled in a desiccator) into a 400-Cc. beaker and dissolve in 50 Cc. of HCl diluted with water. Heat in the covered beaker until dissolved, dilute to 300 Cc. with water and add an excess of Br water. Remove Br by heat, wash the cover and sides of the beaker with water, add an excess of NH_4OH solution and boil gently 15 minutes. Filter into a carefully calibrated 1000-Cc. flask, wash beaker and filter with water containing NH_4OH, then with water several times. Dissolve the precipitate in the least possible amount of HCl, reprecipitate Fe in it with NH_4OH and add the filtrate and washings to the zinc solution. The $Fe(OH)_3$, after washing, is dried, ignited, and the quantity of Fe contained in it deducted from the weight of Zn taken (10 Gm.). If silica or other impurity be found present in the zinc the proper correction for them must be applied. Acidify the alkaline solution, add to it 30 Cc. of HCl together with 10 Gm. NH_4Cl, and dilute to mark on cooling to standard temperature. Pour the solution into a dry, 2-liter bottle, let the flask drain, fill it with distilled water and pouring this into the bottle shake the contents well. Calculate the quantity of Zn contained in 1 Cc. of the V.S. and label the solution accordingly.

Standardization. — To standardize the potassium ferrocyanide V.S. (see p. 167), 20, 50, 70 and 100 Cc. portions of the standard zinc solution are measured into 4 titration flasks and each portion diluted to 150 Cc. with distilled water. Heat the solution to near boiling, reserve about 20 Cc. and titrate the rest with the empirical ferrocyanide V.S., run in from a burette. Add the V.S. in rather larger portions until a drop or two of the titrated liquid give decided color with a drop of the indicator on a white porcelain plate. Add now 18 Cc. of the reserved 20 Cc. portion and run in the V.S., one half Cc. at a time, testing the liquid as before. When a distinct brown color is produced with the indicator, add the remaining 2 Cc. of the zinc solution and complete titration, 2 drops at a time, until a slight excess (pale brown color is produced) of the V.S. is added. Titrate each portion in this manner and find separate factors for each of the volumes of zinc solution titrated.

The exact shade of color of the end-reaction is established by a blank titration in which 10 Cc. of concentrated HCl are neutralized with NH_4OH, the solution acidified with 3 Cc. of HCl in excess, diluted to 150 Cc. and titrated after heating to 85° C. (About 0.2 Cc. of standard K_4FeCN_6 V.S. should be consumed.) Correction for the blank is then applied in all titrations.

When the V.S. is employed in determinations of zinc, the nearest factor to which the volume of the consumed V.S. corresponds, is used in calculation of zinc present.

Empirical Uranium Acetate V.S.[1]

$$UO_2(C_2H_3O_2)_2 \cdot 2H_2O = 424.60.$$
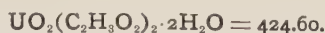
Dissolve about 36 Gm. of pure uranium acetate in water, add 3 Cc. of strong acetic acid and dilute, with distilled water, to measure 1 Lt. Let the solution stand several days and filter. Standardize the solution with a standard solution of an alkali phosphate only when it is to be employed for titration of the soluble phosphates; if to be employed for determination of the alkaline-earth phosphates, calcium phosphate must be used in standardization. There will be then required:

(*a*) *Standard Solution of a Soluble Phosphate.*—This is usually prepared by dissolving 14.7 Gm. of air-dried sodium-ammonium phosphate in water to measure, at standard temperature, exactly 1000 Cc. In place of this salt potassium dihydrogen phosphate has been used, the quantity required being 9.57 Gm. To find its exact strength, fifty Cc. of the solution $(NaNH_4HPO_4 + 4H_2O)$ are evaporated to dryness, the residue ignited and weighed as sodium metaphosphate. 1 Gm. of sodium metaphosphate corresponds to 0.7447 Gm. P_2O_5.

(*b*) *Solution of Ammonium or Sodium Acetate,* 10 per cent. to be prepared when wanted. The solution is acidified with 3 per cent. of acetic acid.

(*c*) *Solution of Potassium Ferrocyanide,* 10 per cent., freshly prepared. In its place the powdered salt may be used as indicator.

Standardization with the Alkali Phosphate.—Transfer to an erlenmeyer flask exactly 30 Cc. of the standard alkali phosphate solution, measuring from burette or with a pipette, add 10 Cc. of the acetate solution, 10 Cc. of water and heat to boiling. Place the flask on a boiling water-bath and having secured the burette containing the uranium acetate solution so that its tip extends into the neck of the erlenmeyer, the burette being at the same time shielded from the heat of the water-bath, titrate the contents of the flask kept hot during the titration. In titration let the uranium solution run into that of the phosphate at the rate of 1 Cc., mixing the contents of the flask and testing for the end-reaction towards the end of the titration. The drop end-point method is employed. Remove a drop of the titrated liquid to a clean porcelain plate and mix it with a drop of the ferrocyanide solution or some of the powdered salt. When a red color is produced the uranium acetate is present in excess. The first should be a trial titration. In the following, more carefully performed titrations, run in a little less of the uranium solution without testing and complete the titration with the V.S., added in 2-drop portions, testing for the end-point after each addition. A drop of the titrated liquid should give a distinct pale brown color with a drop of the indicator. When two or more of the titrations are found to agree within 0.2 Cc., the average of these is taken for calculation of the factor. Since the quantity of P_2O_5 represented by 30 Cc. of the phosphate solution is known, that

[1] Uranium Nitrate V.S. may be used in place of this. Prepared by dissolving 35 Gm. $UO_2(NO_3)_2$ in water to measure 1000 Cc.

quantity of it to which 1 Cc. of the uranium acetate V.S. corresponds, is readily calculated. This factor is to be plainly written on the label of the bottle containing the V.S. The standardized uranium solution may then be used unchanged, or carefully diluted to any suitable volume, so that 1 Cc. may represent a definite quantity of P_2O_5, for instance, 0.005 Gm.

$$Na_2HPO_4 + UO_2(C_2H_3O_2)_2 = UO_2HPO_4 + 2NaC_2H_3O_2.$$
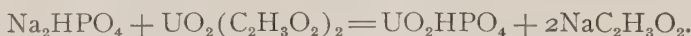
Observations.—The uranium acid phosphate, UO_2HPO_4, or the uranium ammonium phosphate, $UO_2NH_4PO_4$, which is formed in the presence of ammonium salts, dissolve in mineral acids but are insoluble in diluted acetic acid. The object of the addition of the alkali acetate is to react with any inorganic acid present, that is, the inorganic acid in the titrated liquid or HNO_3 generated when uranium nitrate is used in place of the acetate in the V.S. The titration must be performed on the hot solution of the phosphate and it is well to allow sufficient time to elapse before the final endreaction is tried for. The precipitate itself does not react with the indicator. For greater accuracy a blank titration should be made under the conditions of the standardization with all the reagents except the phosphate. The uranium solution should be added, drop by drop, to the hot liquid until a coloration matching exactly that of the determination is produced and the volume of the solution consumed in the blank then allowed for.

Note.—Recently a tincture of cochineal has been used as indicator. The tincture is prepared by boiling 4 Gm. of the dried insect 1 hour in 100 Cc. of water, replacing the water lost and boiling again, then cooling and adding 50 Cc. of alcohol, mixing and filtering. Few drops of the tincture added to the titrated liquid turn to a gray-green color when an excess of the uranium solution is added.

Standardization with Calcium Phosphate.—Pure calcium phosphate is prepared from calcium chloride solution made alkaline with ammonium hydroxide and precipitated with sodium phosphate. The precipitate is washed with hot water, dried, and gently ignited. For standard solution, 5.5 Gm. of the phosphate are digested with diluted sulphuric acid, of which a volume is to be used to contain 2.8 to 2.9 Gm. of SO_3 (adjusted by titration), the solution diluted to 1000 Cc., filtered, and the exact percentage of P_2O_5 present determined gravimetrically. The phosphate may, however, be dissolved in the smallest possible volume of NHO_3 and the solution diluted to exactly 1000 Cc. Of this solution 50 Cc., made alkaline with ammonium hydroxide, evaporated to dryness and ignited, will give a residue of pure calcium phosphate from the weight of which the amount of P_2O_5 present in it is calculated. To titrate the uranium acetate V.S., 50 Cc. of the calcium phosphate solution are measured into an erlenmeyer flask, 10 Cc. of the alkali acetate added and, without heating, the uranium acetate solution introduced in portions until the calcium is nearly all precipitated. The mixture is at this point heated to boiling and the titration completed as in the standardiza-

tion with an alkali phosphate. The exact strength of the uranium acetate solution is then found by calculation, the value of 1 Cc. of it in terms of P_2O_5 being expressed as the factor.

Observation.—The titration of the calcium phosphate must be carried out in the cold, up to a certain point, on account of the tendency of the phosphate to separate out as an acid phosphate, $CaHPO_4$, and also as the tricalcium phosphate, $Ca_3(PO_4)_2$. For this reason the determination of an alkaline-earth phosphate must be carried out under exactly the same conditions obtained in the standardization of the volumetric solution.

Standard Alkaline Cupric Tartrate V.S.
(Fehling's Solution).

1000 Cc. yield 9.939 Gm. of Cu_2O which correspond to 5.0 Gm. of glucose. Prepare and keep in two parts.

A. Of pure copper sulphate (selected crystals) 34.67 Gm., accurately weighed, are dissolved in distilled water to measure exactly 500 Cc. at standard temperature. This portion is to be kept in a glass-stoppered bottle.

B. Sodium potassium tartrate, 173 Gm., and potassium hydroxide, 75 Gm., are dissolved in water to measure exactly 500 Cc., at standard temperature. The solution is kept in a rubber-stoppered bottle.

For use, equal volumes of the two portions are mixed. One Cc. of the V.S. is considered to correspond to 0.005 glucose. This, however, is true only when the determinations with it are carried out strictly under certain fixed conditions. For exact work the solution should be standardized with pure sugar, preferably the kind to be determined, employed in 0.5 per cent. solution.

Standardization of Fehling Solution with Pure Cane Sugar.—Dissolve 4.75 Gm. of pure sucrose in 75 Cc. of distilled water, add 5 Cc. of HCl (1.188 or 38.8 per cent.) and invert the sugar by heating in a water-bath to 70° C., during 2 to 3 minutes, and keeping at 67–69° C. for 7 to 8 minutes longer; heating in all 10 minutes. At 20° C., the inversion is completed in 24 hours; at 25° C. in 10 hours. Neutralize the HCl, exactly, with NaOH solution and dilute to measure, at standard temperature, 1 Lt. One (1) Cc. of this solution will contain 0.005 Gm. of invert sugar and will correspond to 1 Cc. of the Fehling V.S. Titrate 10 Cc. of the Fehling solution with the standard solution of invert sugar in the manner given under titration of glucose (p. 193) and apply a correction if necessary.

Tenth-normal Bromine V.S. (Koppeschaar's Solution).
1000 Cc. contain 7.992 Gm. of Br.

The solution contains a bromate and a bromide in such quantities as to yield 7.992 Gm. of bromine, per 1 Lt., when treated with an acid. A stronger than $\frac{N}{10}$ solution is made by dissolving 3.2 Gm. of pure potassium bromate and 50 Gm. of pure potassium bromide

in distilled water to measure 900 Cc. The solution is then standard-
ized and diluted to $\frac{N}{10}$ strength.

Standardization with $\frac{N}{10}$ Thiosulphate V.S.—Measure into a
suitable, 250-Cc. glass-stoppered bottle, exactly 20 Cc. of the solu-
tion, add 75 Cc. of water, 5 Cc. of pure concentrated HCl, close the
bottle securely and mix contents by shaking. Carefully introduce
5 Cc. of 10 per cent. KI solution so that no Br vapor is lost, close
the bottle at once and agitate the liquid thoroughly. Before titrating
the liberated iodine, rinse the stopper and neck of the bottle with
water into the bottle. Titrate the liquid with $\frac{N}{10}$ thiosulphate, added
in small portions at first, and then in drops until the final yellow
color of the titrated liquid is just discharged by one drop of the
V.S. Dilute each 20 Cc. of the Br solution to a volume exactly
equal to that of the $\frac{N}{10}$ thiosulphate consumed. After dilution, con-
firm the standard of the V.S. by another titration and, if exact, keep
the solution in dark-colored, glass-stoppered bottles. Otherwise,
another adjustment should be made.

INDICATORS.

Only a few indicators are available for use in the precipitation
titrations. They are solutions of inorganic salts; some are added
to the titrated liquids, others are mixed with small portions of them
outside the titration vessel.

AMMONIUM FERRIC SULPHATE SOLUTION (AMMONIUM FERRIC ALUM) $(NH_4)Fe(SO_4)_2 + 12H_2O$.

A saturated solution of the salt in water is employed. The solu-
tion is acidified with a few drops of pure nitric acid for the purpose
of better keeping; the acid at the same time diminishes the intensity
of the red color. About 1 to 2 Cc. of the solution are used in titrations
for 100 Cc. of the titrated liquid, though, when a heavy precipitate
is formed, as much as 5 Cc. are added. The salt, like other ferric
salts, reacts with thiocyanates, giving with them in solution a deep
red color unaffected by dilute acids. The red compound, ferric
thiocyanate, is decomposable by silver nitrate and does not form in
a solution in which $AgNO_3$ is present. But as soon as any silver
contained in a solution is removed, or, has formed an insoluble com-
pound, the slightest excess of a soluble thiocyanate acts on the indi-
cator producing a red color. Titrations with this indicator are
carried out in the presence of nitric acid which prevents precipita-
tion of Ag by other anions. In addition, HNO_3 causes the silver
compound precipitated to separate more readily.

POTASSIUM CHROMATE SOLUTION (K_2CrO_4).

A ten (10) per cent. solution of the pure salt in distilled water
is prepared. Being used in titration of halogen compounds, the
indicator must be free from chloride, its common impurity. Ab-
sence of chloride is readily established by a silver nitrate solution
added to a portion of the salt dissolved in distilled water; the red

precipitate formed should dissolve to a *clear* solution in nitric acid added subsequently. With silver nitrate, potassium chromate gives a red precipitate of silver chromate, soluble in acids, alkalies and decomposable by $AgNO_3$. This compound, therefore, forms only in absolutely neutral solutions and then only when any haloid salt present has reacted with the silver. The solutions titrated in presence of this indicator must be neutral and must be so maintained during titration. For this purpose Na_2CO_3 can be used, as a slight excess of it present does not interfere; but MgO, free from chloride, is better suited and more commonly employed. An excess of this compound has no undesirable action.

Sodium arsenate solution has been used (Lunge), in place of potassium chromate, as indicator.

POTASSIUM FERROCYANIDE SOLUTION ($K_4FeCN_6 \cdot 3H_2O$).

The solution, ten per cent. strong, should be made when wanted. This indicator is employed for the drop end-reactions. When so used, one drop of it is mixed with a drop of the titrated liquid on a clean, white porcelain plate. With ferric compounds it gives a deep blue, with uranium salts a red-brown color. In place of the solution, the powdered salt has been employed.

POTASSIUM IODIDE SOLUTION (KI).

A 10 per cent. solution of pure KI in distilled water.

URANIUM ACETATE SOLUTION, $UO_2(C_2H_3O_2)_2 + 2H_2O$.

The volumetric solution of this salt, see p. 169, will be found to answer this purpose. The indicator serves to detect the presence of ferrocyanide in the titrated liquid, the drop end-point method of testing being used. In place of the uranium solution, ferric chloride solution in glacial acetic acid can be used. With ferrocyanide a deep blue color is produced.

Titrations with Standard Silver Nitrate V.S.—Titrations with standard silver nitrate V.S. are carried out in several ways:

I. Direct Titration Without Indicator. (Method of Gay-Lussac.)

The titrated liquid may contain nitric acid; the V.S. is added carefully in portions until it ceases to produce a precipitate. For exact results two V.S., strong and weaker, are employed, the titration being completed with the weaker solution.

II. Direct Titration in Presence of an Indicator. (Mohr's Method.)

The liquid to be titrated must be absolutely neutral in reaction and its neutrality maintained during the titration. In titration, the indicator, potassium chromate solution, is added and the V.S. run in until, in addition to the haloid salt of silver first formed, a red precipitate of silver chromate is produced. The red color of the end-reaction must be looked for in the precipitate. Metals which

react with the indicator in neutral solutions, as well as acid radicles that form insoluble salts with silver, must be absent.

III. Residual Titration.   (Volhard's Method.)

An additional V.S. of standard thiocyanate is employed and the solution of ammonium ferric sulphate used as indicator.   To the solution of the sample, acidified with nitric acid, is added the standard $AgNO_3$ V.S. in excess or until it produces no further precipitation; the excess of the silver added is found by titration with the thiocyanate V.S.   The end-reaction depends on the formation of a red-colored ferric thiocyanate which appears only when all the silver has been precipitated as AgSCN.   When the two standard V.S. are of exactly the same equivalent strength, preferably the tenth-normal, the volume of the silver nitrate V.S. consumed by the sample is obtained by simple subtraction.

IV. Cyanide Titration.   (Method of Liebig.)

An alkali cyanide is titrated with standard silver nitrate, the V.S. being added until a slight precipitate appears.   This precipitate of AgCN appears only when the alkali cyanide present is all converted into a soluble double cyanide of alkali and silver.   To increase the sharpness of the end-reaction, a small quantity of KI solution is added to act as indicator, the AgI separating at this point more readily.   In this titration the $\frac{N}{10}$ silver nitrate V.S. has the value of $\frac{N}{5}$ V.S., a fact which must, of course, be considered in calculation of the results of a titration in this manner.

Cyanide can also be titrated in neutral solutions, with potassium chromate as indicator, the titration differing in no respect from that of the halogens given under Mohr's method.

In all these titrations the coloration of the end-reaction is not very intense so that the proper background for its observation should be provided.   See p. 8.

1.   Determination of Halogens in Soluble Binary Compounds.

A. Direct Titration.   (Mohr.)

Chloride,[1] bromide and iodide.
Volumetric solution employed: $\frac{N}{10}$ silver nitrate.
Indicator: Potassium chromate solution.

Dry the sample at 100° C., during 1 hour, and let cool in a desiccator.   For one titration employ 0.15 to 0.3 Gm. of the dry sample. Weigh accurately, dissolve in water to measure 10 to 20 Cc. (if an iodide, 200 Cc.) in a titration flask, add 1 Gm. of chloride-free MgO, then 2 drops of the indicator and titrate with the $\frac{N}{10}$ $AgNO_3$ V.S. In titration, add the V.S. in small portions with effective agitation of the titrated liquid, reducing the flow to drops toward the end of the operation.   Finally one drop of the V.S. should be found to

[1] If mercuric chloride, Hg must be removed (by H_2S, etc.), silver chloride being soluble in mercuric nitrate.

produce a distinct, reddish precipitate of silver chromate. This compound forms only when all of the halogen present has combined with the silver and is seen in the white or yellowish silver salt precipitated before it. From the results of two or more agreeing titrations, the average volume of $\frac{N}{10}$ silver nitrate V.S. consumed is taken, and the percentage of the particular salt present or of the halogen contained in it is calculated. For derivation of the required factors the equation representing the reaction between NaBr and $AgNO_3$ is here given to serve as a type for other halogen compounds:

$$\underset{102.92}{NaBr} + \underset{169.89}{AgNO_3} = AgBr + NaNO_3.$$

The equation shows that 169.89 parts of $AgNO_3$ react with 102.92 parts of NaBr, which contain 79.92 parts of bromine. Since 1 Lt. of $\frac{N}{10}$ $AgNO_3$ contains 16.989 Gm., and corresponds to 10.292 Gm. of NaBr,

1 Cc. of the V.S. is the equivalent of 0.010292 Gm. of sodium bromide, or of 0.007992 Gm. of bromine.

Illustration.—A sample of sodium bromide, titrated in 0.2 Gm. portions, required an average of 19.2 Cc. of $\frac{N}{10}$ $AgNO_3$ V.S.; to calculate the percentage of NaBr in the sample.

$$19.2 \times 0.010292 = 0.1976 \text{ Gm.}$$

$$0.2 : 0.1976 :: 100 : x.$$

$$x = \frac{0.1976 \times 100}{0.2} = 98.8.$$

The sample is found to contain 98.8 per cent. of NaBr.

Observations.—The red Ag_2CrO_4 is formed only in neutral solutions and being insoluble under these conditions appears in the precipitated haloid salt of silver. Magnesium oxide is added to maintain neutrality, an excess of it not interfering with the end-reaction. It is evident that in neutral solutions other anions (phosphate, oxalate, arsenite, arsenate, etc.), if present, would react with silver nitrate. In the presence of these and other interfering substances this method of titration can not be carried out and recourse is had to the Volhard method. Considerable dilution of the solution of an iodide is necessary to prevent adsorption of the dissolved iodide or the added silver nitrate.

B. *Residual Titration.* (Volhard.)

Volumetric solutions employed: $\frac{N}{10}$ silver nitrate and $\frac{N}{10}$ thiocyanate.

Indicator: Ammonium ferric sulphate solution.

To 0.1 or 0.2 Gm. of the sample, dissolved in 10 to 20 Cc. of distilled water, add the $\frac{N}{10}$ $AgNO_3$ V.S. in portions, mixing well, until an excess is added, that is, until a precipitate no longer forms. Add to the mixture 1 Cc. of the indicator, 5 Cc. of pure, 10 per cent.

HNO_3, and mix the contents of the flask thoroughly. If the haloid salt determined is a chloride, filter, wash the precipitate with water containing a few drops of nitric acid, combine the filtrate with washings and titrate with the $\frac{N}{10}$ thiocyanate V.S. Add the V.S. with due care, in small portions, agitating well, and reducing the flow toward the end so that one drop of it, finally added, shall produce a distinct reddish or pink color, which does not disappear on mixing. With the other halogens, titrate the unfiltered mixture in the same manner. Both V. solutions being tenth-normal, the Cc. of the thiocyanate V.S. consumed are deducted from the Cc. of silver nitrate V.S. added and, from the difference, which constitutes the Cc. of $\frac{N}{10}$ silver nitrate V.S. consumed by the haloid salt, the percentage of the salt or of the halogen it contains is calculated. Equations which give the factor required are:

$$\underset{74.56}{KCl} + \underset{169.89}{AgNO_3} = AgCl + KNO_3.$$

$$AgNO_3 + KSCN = AgSCN + KNO_3.$$

169.89 parts of $AgNO_3$ are represented reacting with 74.56 parts of KCl which contain 35.46 parts of Cl.

1 Lt. of $\frac{N}{10}$ $AgNO_3$ contains 16.989 Gm., and corresponds to 7.456 Gm. of KCl.

1 Cc. is the equivalent of 0.007456 Gm. of potassium chloride, or of 0.003546 Gm. of chlorine.

Observations.—The residual method permits titration of the haloid salts in the presence of those compounds which interfere in neutral solutions. The nitric acid which is added to the titrated liquid should be free from nitrous acid. It should be carefully noted that the nitric acid and the indicator are both added after an excess of the $\frac{N}{10}$ $AgNO_3$ V.S. has been introduced. This practice is necessary particularly in titration of an iodide, both nitric acid and ammonium ferric sulphate being capable of liberating iodine from a soluble iodide, though they do not react with the silver iodide. The precipitated AgCl is removed by filtration to prevent a reverse action, viz.:

$$AgCl + NH_4SCN = AgSCN + NH_4Cl \text{ and } AgCl + Fe(SCN)_3$$
$$= AgSCN + FeCl_3,$$
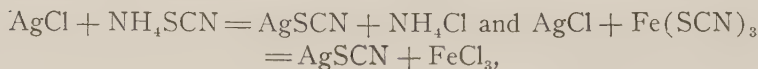
which would otherwise take place. On account of these reactions taking place the results, without such removal, would be low and the end-reaction uncertain. The iodide and bromide of silver, not reacting in this manner, need not be removed.

Notes.—(*a*) *Ternary Haloid Salts* may be determined by this method of titration after reduction. As the reducing agent nascent hydrogen may be used, but hydroxylamine sulphate has been found very efficient. To reduce a portion of a sample with this reagent, to about 0.25 Gm. of it, dissolved in 50 Cc. of water, 5 Gm. of solid hydroxylamine sulphate and an excess of nitric acid are added. After warming, the solution is titrated by Volhard's method. Am-

monium hydroxide is often used in place of nitric acid for the reduction, it being of special value in the reduction of iodates. In that case the solution, after reduction, is made acid with nitric acid and titrated.

(b) *Halogens in Nonelectrolytes* must be combined to a metal before they can be titrated. Few methods, out of many, will be here suggested.

1. A portion (0.1 to 0.2 Gm.) of the sample to be determined is weighed in a small glass tube, placed with the tube in an erlenmeyer flask, 20 to 40 Cc. of 98 per cent. alcohol added, and the contents heated on water-bath under a return condenser (fig. 29). Small pieces of metallic sodium are dropped in, through the condenser tube, until 20 times the theoretical amount of Na, required for the halogen present, are added (one atom of the halogen requires 2 of Na). After the added sodium has dissolved, 20 to 40 Cc. of distilled water are introduced, and the alcohol removed by distillation. The solution which remains is cooled, acidified with HNO_3, and the halogen now present in combination with sodium, determined by the Volhard method of titration. This method is of general application.

2. A weighed portion of the nonelectrolyte is heated in a sealed tube with an excess of $AgNO_3$ and strong nitric acid (method of Carius). After decomposition, the halogen is found combined to silver; the unconsumed $AgNO_3$ is determined by titration of the diluted mixture with standard thiocyanate V.S. In another method the substance is decomposed by heating with pure lime in a combustion furnace, the ignited mass dissolved in dilute nitric acid and the halogen in solution determined by titration with $\frac{N}{10}$ silver nitrate V.S. Heating with powdered aluminium, or with alcoholic potassium hydroxide, under return condenser, is also practiced.

2. Determination of Chloral, Chloroform, Trichloracetic Acid.

A portion (0.3 Gm.) of the sample is accurately weighed into a suitable erlenmeyer, mixed with 60 Cc. of distilled water, 2 Gm. of powdered aluminium are added and the contents heated under a return condenser, boiling during 20 minutes. After cooling, the Al in excess is dissolved in acetic acid, the solution filtered and, in the filtrate, the halogen titrated by Volhard's method. From the volume of $\frac{N}{10}$ $AgNO_3$ V.S. consumed by the halogen, the quantity of the organic compound determined is calculated.

1 Cc. $\frac{N}{10}$ $AgNO_3$ V.S. is the equivalent of 0.00398 Gm. of chloroform, or 0.005514 Gm. of chloral hydrate, or 0.005446 Gm. of trichloracetic acid, or 0.003848 Gm. of carbon tetrachloride.

3. Determination of Iodoform.   (In dressings.)

The sample weighing 5 to 6 Gm., is extracted, by maceration, with ether-alcohol (150 Cc.) in a glass-stoppered bottle during 1 to 2 hours with occasional shaking. One third (50 Cc.) of the ethereal solution is drawn off by means of a pipette, transferred to a flask and heated with 50 Cc. of $\frac{N}{10}$ $AgNO_3$ V.S. and 5 Cc. of 10

13

per cent. HNO_3 under return condenser, at water-bath temperature, during 20 minutes. After that the ether and alcohol are removed by distillation, the residual liquid diluted with water, ammonium ferric sulphate added, and the excess of $AgNO_3$ titrated with $\frac{N}{10}$ thiocyanate V.S. From the volume of silver nitrate V.S. consumed by the iodine of the iodoform, the percentage of CHI_3 in the sample is calculated.

$$\underset{393.77}{CHI_3} + \underset{3 \times 169.89}{3AgNO_3} + 2H_2O = 3AgI + 3HNO_3 + CO_2.$$
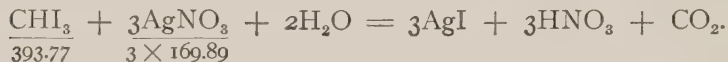
1 Cc. of $\frac{N}{10}$ $AgNO_3$ V.S. is the equivalent of 0.013126 Gm. of iodoform.

4. Determination of Acetone. (J. M. Auld.)

Acetone is converted into $CHBr_3$ by bromine, the product is distilled, decomposed by an alkali and the bromide produced titrated with standard silver nitrate V.S.

Volumetric solution required: $\frac{N}{10}$ silver nitrate.

Indicator: Potassium chromate solution.

Into a 500 Cc. flask is placed 0.1–0.2 Gm. of acetone or as much of a solution of it as will contain so much acetone, a little water, and 20–30 Cc. of 10 per cent. KOH solution are added and the flask connected with a return condenser. Through the tube (which should be straight) of the condenser (fig. 29), a solution of bromine in potassium bromide (Br 20, KBr 25 + H_2O, q. s., to make 100 Cc.) is rapidly dropped in until a permanent yellow color is imparted to the solution. The contents of the flask are then heated on water-bath at 70° C., during one half hour. The color of free bromine, which should be only in small excess, is discharged by the addition of KOH, and the $CHBr_3$ is distilled into a 100 Cc. flask. If the contents of the flask are low some water should be added before distillation. After distillation, the condenser tube is washed out with alcohol, 50 Cc. of alcohol and enough KOH to constitute 10 per cent. added, and the contents heated under return condenser during forty-five minutes, or until the saponification is complete. The liquid is then evaporated to near dryness, the residue taken up with water, free alkali exactly neutralized with dilute nitric acid, water added to make the solution measure a definite volume. Aliquots are then measured out for titration with $\frac{N}{10}$ $AgNO_3$ in the presence of potassium chromate solution as indicator. To maintain neutrality some MgO should be added. From the volume of $\frac{N}{10}$ $AgNO_3$ V.S. consumed by bromide obtained from the quantity of acetone taken and changed into $CHBr_3$, the percentage of acetone in sample is calculated. Reactions:

1. $\underset{58.06}{C_3H_6O} + 6Br + 4KOH$

$\qquad = CHBr_3 + KC_2H_3O_2 + 3KBr + 3H_2O.$

2. $$3CHBr_3 + 9KOH + C_2H_5OH$$
$$= 3CO + C_2H_4 + \underset{9 \times 79.92\,(Br.)}{9KBr} + 7H_2O.$$

3. $$KBr + AgNO_3 = AgBr + KNO_3.$$
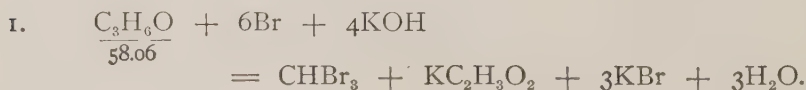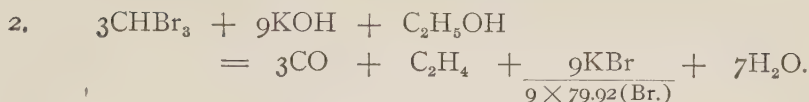
One acetone (58.06) gives $CHCl_3$ which gives $3KBr$, containing 3×79.92 Br, and reacting with 3×169.89 Gm. $AgNO_3$.

1 Lt. of $\frac{N}{10} AgNO_3$ V.S. contains 16.989 Gm., and corresponds to $\frac{58.06}{3}$ Gm. acetone.

1 Cc. of the V.S. is the equivalent of 0.001602 Gm. of acetone.

5. Chloride and Bromide Together.

Of the sample, 1 to 2 Gm. are dissolved in 150 to 200 Cc. of distilled water, 2 to 3 Cc. of 10 per cent. solution of ammonium persulphate added and the solution heated to between 70° and 80° C. until all the bromine is driven off. When free from Br, the solution is made to measure a definite volume by the addition of water, and the chloride in it determined by titration of aliquot portions with $\frac{N}{10} AgNO_3$ V.S. In another solution of 0.2 to 0.5 Gm. of the sample both halogens are titrated with $\frac{N}{10}$ silver nitrate V.S. Since the volume in Cc. of $\frac{N}{10} AgNO_3$ V.S. consumed in the first titration corresponds to the chloride, when this is subtracted from the Cc. of the V.S. required for the same quantity of the sample in the second, the difference represents the volume in Cc. of the V.S. which corresponds to the bromide. From these data the calculation of the percentage of each ingredient is then readily performed.

6. Chloride and Iodide Together.

About 1 Gm. of the sample, accurately weighed, is dissolved in 100 Cc. of distilled water, the solution heated to boiling with an excess of ammonium ferric sulphate until all iodine is liberated and removed. The iodine-free liquid is titrated by Volhard's method to determine the chloride.

Both halogens are titrated in another portion of the sample (0.2 to 0.3 Gm.), and the volume of $\frac{N}{10} AgNO_3$ V.S. consumed, noted. The Cc. of the V.S. consumed by the chloride in an equal quantity of the sample subtracted from Cc. of $\frac{N}{10} AgNO_3$ V.S. consumed by both, gives the volume of the V.S. which corresponds to the iodide.

From these data the percentage of each ingredient in the mixture is calculated in the usual manner.

7. Chloride, Bromide and Iodide Together.

In a weighed quantity of the sample, dissolved in distilled water, the iodide is decomposed by sodium nitrite and diluted sulphuric acid and the iodine either removed by heating, in which case the liquid is titrated for Cl + Br, or distilled into KI solution for titration. The bromide in the I-free solution is decomposed by per-

manganate (5 per cent. solution) and the Br distilled into KI solution for titration or the residual liquid titrated for chloride. Chloride is found by difference or may be determined by titration after the other halogens have been removed.

8. DETERMINATION OF HCN AND THE SOLUBLE CYANIDES.   (Liebig.)

Cyanides in alkaline solutions form soluble double cyanides with silver which are decomposed by an excess of the silver, AgCN precipitating.

Volumetric solution employed: $\frac{N}{10}$ silver nitrate.

Indicator: Potassium iodide solution.

Accurately weigh 5 Cc. of the solution of dilute hydrocyanic acid or 0.5 Gm. of a soluble cyanide into the titration flask, dissolve in water and dilute to measure 20 Cc. Add to the solution 5 Cc. of 10 per cent. ammonium hydroxide, 5 drops of 10 per cent. KI solution and titrate with the $\frac{N}{10}$ silver nitrate V.S. Add the V.S. carefully, in small portions, mixing well after each addition until a yellowish precipitate or turbidity is produced by one drop of the V.S. Having made a check titration, calculate, from the volume of the V.S. consumed, the percentage of the acid or of the particular cyanide in the sample. The factor for HCN with $\frac{N}{10}$ V.S. is found from the following equations:

$$HCN + NH_4OH = NH_4CN + H_2O.$$

$$\underset{2 \times 27.01\,(HCN)\,+\,169.89}{2NH_4CN \ + \ AgNO_3} \ = \ AgCN \cdot NH_4CN \ + \ NH_4NO_3.$$

169.89 parts of $AgNO_3$ react with 2×27.01 parts of HCN in form of NH_4CN.

1 Lt. of $\frac{N}{10}$ $AgNO_3$ contains 16.989 Gm., and corresponds to 5.402 Gm. HCN.

1 Cc. of the V.S. is the equivalent of 0.005402 Gm. of hydrocyanic acid.

Observations.—The end-reaction depends on the precipitation of AgI which forms according to the equation:

$$KI + AgNO_3 = AgI + KNO_3,$$

as soon as all the cyanide present is converted into the soluble double cyanide of alkali and silver. Since two molecules of the cyanide are present in this compound, and therefore are consumed by one silver, the $\frac{N}{10}$ silver nitrate V.S. has the value of a $\frac{N}{5}$ V.S. in this titration. The ammonium hydroxide is added to the HCN to form NH_4CN with the acid and would appear to be unnecessary in the case of a cyanide. It is, however, added to alkali cyanides to overcome the hydrolytic action of water which is considerable. Insoluble cyanides are decomposed by an acid and the generated HCN distilled into an excess of an alkali for titration.

Total HCN in ferrocyanides may also be determined by distil-

lation.[1]   The sample is first heated with 10 Cc. of N–NaOH, then 15 Cc. of hot 3N magnesium chloride solution added, the mixture boiled 5 minutes and, after the addition of 100 Cc. of $\frac{N}{10}$ mercuric chloride solution, the boiling is continued 10 minutes longer.   The flask is then connected with a distillation apparatus and the contents decomposed with 30 Cc. 4N sulphuric acid and the HCN generated distilled into 25 Cc. of N–NaOH.   After distillation, the contents of the receiver are diluted to 400 Cc. and titrated with $\frac{N}{10}$ silver nitrate, using KI as indicator.

9. Determination of Thiocyanate.

Volumetric solutions employed : $\frac{N}{10}$ silver nitrate and $\frac{N}{10}$ thiocyanate. Indicator : Ammonium ferric sulphate solution.

To a suitable portion of the sample (0.2 to 0.3 Gm.), dissolved in 20 Cc. of distilled water, add the $\frac{N}{10}$ AgNO$_3$ V.S. in portions until an excess has been added.   Drop in 1 Cc. of the indicator, acidify with 5 Cc. of 10 per cent. HNO$_3$ and titrate with the $\frac{N}{10}$ thiocyanate V.S. to the appearance of a permanent reddish color produced by a final drop of the V.S.   From the volume of $\frac{N}{10}$ silver nitrate consumed by the sample the percentage of the thiocyanate in it is obtained by calculation.   In another method of titration, 10 to 20 Cc. of $\frac{N}{10}$ AgNO$_3$ V.S. are carefully measured into a titration flask, 5 Cc. of 10 per cent. HNO$_3$ and 0.5 Cc. of the indicator added and the solution titrated with a solution of the sample, the exact strength of which is known.   In this, as in the other titration, a distinct and permanent reddish color, produced by one drop of the solution finally added, indicates the end of the reaction.   From the volume of the solution of the sample required to react with a given volume of $\frac{N}{10}$ AgNO$_3$ V.S. the percentage of the thiocyanate present is calculated.

$$\underset{76.13}{NH_4SCN} \; + \; \underset{169.89}{AgNO_3} \; = \; NH_4NO_3 \; + \; AgSCN.$$

169.89 parts of AgNO$_3$ react with 76.13 parts of NH$_4$SCN.   Since 1 Lt. of $\frac{N}{10}$ AgNO$_3$ contains 16.989 Gm., and corresponds to 7.613 Gm. of NH$_4$SCN,

1 Cc. of the V.S. is the equivalent of 0.007613 Gm. of ammonium thiocyanate, or of 0.005908 Gm. of thiocyanic acid.

10. Cyanide and Thiocyanate Together.

The solution of a suitable quantity of the sample is made alkaline with KOH diluted to 100 Cc. and titrated with $\frac{N}{10}$ AgNO$_3$ V.S. to the production of a precipitate.   From the volume of the V.S. thus consumed the proportion of the cyanide is calculated.   See cyanides, No. 8.   The V.S. is then added in excess, the mixture acidified with 10 per cent. HNO$_3$, mixed well, filtered, and the precipitate washed with acidified water.   In the filtrate and washings combined, the excess of the AgNO$_3$ is determined by titration with $\frac{N}{10}$ thiocyanate, using ammonium ferric sulphate solution as indicator.   The

[1] Analyst, 1908, 388, p. 261.

total volume of $\frac{N}{10}$ silver nitrate consumed by the sample, less twice the Cc. of it used for the cyanide, gives the volume which corresponds to the thiocyanate. From this the percentage of the thiocyanate in the sample is calculated. See No. 9.

11. Chloride, Cyanide and Thiocyanate Together.

A portion of the sample, dissolved in water, is titrated for the cyanide by Liebig's method. The volume of $\frac{N}{10}$ AgNO$_3$ V.S. consumed may be represented by $= a$.

To another equal portion, acidified with nitric acid, is added $\frac{N}{10}$ AgNO$_3$ in excess, the mixture well shaken and filtered, the precipitate washed and the filtrate and washings combined and titrated with $\frac{N}{10}$ thiosulphate V.S. The volume of $\frac{N}{10}$ AgNO$_3$ V.S. consumed corresponds to all three, represented by $= b$.

The precipitate is then transferred to a flask and boiled with concentrated HNO$_3$ (1.4) during 45 minutes to oxidize the cyanide and thiocyanate, the mixture diluted to 100 Cc., a solution of Ba(NO$_3$)$_2$ added to precipitate the sulphate formed, and the clear liquid, without filtering, titrated with $\frac{N}{10}$ thiocyanate V.S. and ammonium ferric sulphate solution as the indicator. The volume of $\frac{N}{10}$ V.S. consumed corresponds to the cyanide and thiocyanate designated as $= c$.

From these data the percentage of each ingredient is then calculated in the usual manner. It will be seen that $b - c =$ the volume of $\frac{N}{10}$ V.S. corresponding to the chloride, and $c - a$ gives the volume of the V.S. corresponding to the thiocyanate present.

12. Determination of Chlorate and Bromate. (Scholtz.)

The ternary compounds containing halogens are reduced to the corresponding binary salts by a nitrite in the presence of nitric acid.

Volumetric solutions employed: $\frac{N}{10}$ silver nitrate and $\frac{N}{10}$ thiocyanate. Indicator: Ammonium ferric sulphate solution.

For each titration 0.25 to 0.4 Gm. of the sample is to be taken. The accurately weighed portion is dissolved in 100 Cc. of distilled water, 10 Cc. of HNO$_3$ (sp. gr. 1.2) added, then 10 Cc. of 10 per cent. NaNO$_2$ introduced and the mixture allowed to stand, at room temperature, during 15 minutes. After complete reduction an excess of $\frac{N}{10}$ silver nitrate V.S. is run in (about 40 Cc.), 5 Cc. of the indicator are added and the mixture filtered, if a chlorate be treated. In the filtrate and washings the excess of silver is titrated with $\frac{N}{10}$ thiosulphate V.S. Reduced bromate requires no filtration. From the volume of the $\frac{N}{10}$ AgNO$_3$ consumed by the sample, the percentage of the particular salt present is calculated.

$$\underset{122.56}{\underline{KClO_3}} + 3HNO_2 = KCl + 3HNO_3.$$

$$KCl + \underset{169.89}{\underline{AgNO_3}} = AgCl + KNO_3.$$

169.89 parts of AgNO$_3$ react with the chloride resulting from 122.56 parts KClO$_3$.

1 Lt. $\frac{N}{10}$ AgNO$_3$ contains 16.989 Gm., and corresponds to 12.256 Gm. of KClO$_3$.

1 Cc. of the V.S. is the equivalent of 0.012256 Gm. of potassium chlorate, or of 0.016702 Gm. of potassium bromate.

Factors for other salts are derived in the same way.

Observations.—No heat is required to bring about the reduction. The excess of the nitrous acid, although it is claimed to be without effect on the results of the titration, is best destroyed by a dilute solution of permanganate. The solution is added up to the production of a distinct pink color which is then discharged by a drop or two of the nitrite solution. If a chloride be present in the sample, it is determined by titration of a separate portion by Volhard's method and the quantity of it found, allowed for in the calculation of the percentage of the chlorate or bromate. Chloride may also be titrated in the same portion with the chlorate by titration according to Mohr's method, previous to reduction. When in this titration the red color of the end-reaction appears, nitric acid and the nitrite solution are added and the method above given followed. The volume of the V.S. consumed in titration before reduction corresponds to the chloride; that consumed in titration after the reduction corresponding to the chlorate. The reduction of bromate is more rapid and titration may be proceeded with after 5 minutes' digestion. Unless the nitrite is known to be entirely free from chloride a blank titration of it should be made and correction applied.

13. CHLORATE, BROMATE AND IODATE. (Brunner and Mellet.)

Reduction to binary compound is effected by formaldehyde and a persulphate, the halogen being in each case determined by Volhard's titration.

Volumetric solutions required: $\frac{N}{10}$ silver nitrate and $\frac{N}{10}$ thiocyanate.

Indicator: Ammonium ferric sulphate.

To 0.1 Gm. of the sample, dissolved in 20 Cc. of water, 10 to 20 Cc. of accurately measured $\frac{N}{10}$ silver nitrate V.S. are added, the mixture acidified with 5 Cc. of nitric acid (1.4), 1 Gm. of K$_2$S$_2$O$_8$ and 1 Cc. of 40 per cent. formaldehyde introduced, and the mixture heated on water-bath until the odor of formaldehyde has disappeared. With iodate, 2 Gm. of the persulphate and 5 Cc. of the formaldehyde are used, and the mixture heated over direct flame. After complete reduction the solution is cooled, 5 Cc. of the indicator added and the excess of AgNO$_3$ titrated with $\frac{N}{10}$ thiocyanate V.S. Calculation of percentage is based on the volume of the $\frac{N}{10}$ silver nitrate V.S. consumed by the sample taken, the factors required being derived as illustrated under the method of Scholtz.

14. DETERMINATION OF HYDROGEN SULPHIDE AND THE SOLUBLE SULPHIDES.

The sulphide in solution is brought into reaction with an excess of standard silver nitrate V.S. and the excess of the V.S. determined by titration.

Volumetric solutions required: $\frac{N}{10}$ silver nitrate and $\frac{N}{10}$ thiocyanate.

Indicator: Ammonium ferric sulphate.

Into a 200 Cc. bottle, provided with a well-fitting stopper, are measured 20 to 50 Cc. of the $\frac{N}{10}$ AgNO$_3$ V.S., a suitable volume of the sulphide solution which should be free from halogens and other silver-precipitating compounds, is added, and the contents thoroughly shaken. The mixture is then diluted, with water, to measure to a definite volume, allowed to stand until the precipitate deposits, and then aliquot portions of the clear liquid are drawn off for titration of the unconsumed AgNO$_3$ with the $\frac{N}{10}$ thiocyanate V.S. From the volume of $\frac{N}{10}$ AgNO$_3$ V.S. consumed by the sample, the percentage of the dissolved sulphide or H$_2$S present is calculated.

$$\underset{2 \times 169.89 + 34.09}{2\text{AgNO}_3 \; + \; \text{H}_2\text{S}} \; = \; \text{Ag}_2\text{S} \; + \; 2\text{HNO}_3.$$

1 Cc. of $\frac{N}{10}$ silver nitrate is the equivalent of 0.0017045 Gm. of H$_2$S.

In the presence of halogens or other substances reactive with silver, the H$_2$S is distilled into an excess of standard silver nitrate V.S. made alkaline with ammonium hydroxide. Soluble sulphides, or other decomposable sulphides, are heated with acetic acid and the H$_2$S evolved, passed into the alkaline AgNO$_3$. When the distillation is completed, the Ag$_2$S precipitate is filtered off, washed, dissolved in HNO$_3$, the solution evaporated, the residue dissolved and the solution of silver nitrate thus obtained titrated with $\frac{N}{10}$ thiocyanate V.S. From the quantity of silver found the percentage of H$_2$S or of the sulphides treated is calculated.

15. Determination of Silver. I. (Mohr.)

An excess of a standard sodium chloride solution is added to precipitate all the silver present, and the unconsumed NaCl is titrated with standard AgNO$_3$ V.S.

Volumetric solutions employed: $\frac{N}{10}$ sodium chloride and $\frac{N}{10}$ silver nitrate.

Indicator: Potassium chromate.

Accurately weigh about 0.5 Gm. of the sample, dissolve in 10 Cc. of distilled water, or if a solution, measure of it that volume which will contain approximately as much AgNO$_3$, neutralize the solution if necessary with MgO and, from a burette, run in an excess of the $\frac{N}{10}$ NaCl V.S. (about 35 Cc.). Mix the contents of the flask well, add 3 to 4 drops of the indicator and titrate with the $\frac{N}{10}$ silver nitrate V.S. Add the V.S. in small portions under constant agitation until one drop of it finally produces a permanent reddish color to be seen in the precipitated AgCl. To confirm the accuracy of the titration another or several should be carried out. Since the V. solutions employed are both of the tenth-normal strength, the Cc. of silver nitrate V.S. consumed are simply subtracted from the Cc. of the $\frac{N}{10}$ NaCl added and, from the difference, which represents the volume of $\frac{N}{10}$ NaCl V.S. consumed by

the sample, the percentage of silver found is calculated. The factor for Ag with $\frac{N}{10}$ V.S. is derived from the equation:

$$\underset{169.89}{\underline{AgNO_3}} + \underset{58.46}{\underline{NaCl}} = AgCl + NaNO_3.$$

58.46 parts of NaCl react with 169.89 parts of $AgNO_3$ which contain 107.88 parts of Ag.

1 Lt. of $\frac{N}{10}$ NaCl contains 5.846 Gm., and corresponds to 16.989 Gm. of $AgNO_3$.

1 Cc. of the V.S. is the equivalent of 0.016989 Gm. of silver nitrate, or of 0.010788 Gm. of metallic silver.

To calculate:

$$\frac{Cc.\ of\ \frac{N}{10}\ NaCl\ consumed \times 0.010788 \times 100}{Weight\ of\ sample} = per\ cent.\ of\ Ag.$$

Observation.—The solution of the sample should be neutral in reaction and should not contain interfering metals such as Pb, Bi, Sb and Hg (ous).

16. Determination of Silver. II. (Volhard.)

Volumetric solution employed: $\frac{N}{10}$ thiocyanate.

Indicator: Ammonium ferric sulphate solution.

The titration for determination of silver is carried out in the manner given for the standardization of $\frac{N}{10}$ thiocyanate with $\frac{N}{10}$ silver nitrate V.S. On account of the large quantity of AgSCN formed, the end-reaction lacks sharpness. To overcome this, the mixture is filtered when nearly all of the silver present is precipitated and, after washing the precipitate with a very dilute HNO_3, the filtrate and washings combined, are titrated with the $\frac{N}{10}$ thiocyanate V.S. and ammonium ferric sulphate as indicator. One drop of the V.S. should finally produce a distinct, permanent reddish color.

$$\underset{169.89}{\underline{AgNO_3}} + \underset{97.18}{\underline{KSCN}} = AgSCN + KNO_3.$$

97.18 parts of KSCN react with 169.89 parts of $AgNO_3$ containing 107.88 parts of Ag.

1 Lt. of $\frac{N}{10}$ KSCN contains 9.718 Gm., and corresponds to 16.989 Gm. of Ag.

1 Cc. of the V.S. is the equivalent of 0.016989 Gm. of silver nitrate, or of 0.010788 Gm. of metallic silver.

Observations.—Copper may be present to the extent of 60 per cent. but not more. If in excess of this proportion its reduction may be brought about through the addition of pure silver, or of silver nitrate, the quantity added being accurately weighed. Otherwise the precipitate obtained with an empirical thiocyanate V.S. is filtered off, washed, transferred to an erlenmeyer flask and decom-

posed by boiling with HNO_3 (1.4) during 45 minutes. After the sulphate produced in the reaction is separated from the solution by the careful addition of $Ba(NO_3)_2$ solution, the silver is titrated, without filtering off the $BaSO_4$, with the $\frac{N}{10}$ thiocyanate V.S.

Organic compounds containing silver are burned and ignited in a porcelain or silica crucible, the residue dissolved in dilute nitric acid, the solution diluted and titrated.

17. Assay of Silver.

For very accurate determination of silver (testing of silver alloys) the method of Gay-Lussac, in which the silver is titrated in an acid solution with standard sodium chloride V.S. without an indicator, is employed. Two empirical V.S. of chemically pure NaCl are needed; one is prepared of such strength that 1000 Cc. of it are required to nearly completely precipitate 5 Gm. of pure silver in solution in HNO_3; the other is made exactly one tenth as strong by a careful dilution of the first with distilled water. The exact strength of these solutions is established by titration with 0.5 Gm. of pure silver.[1] The pure silver is dissolved in nitric acid (1.2), the solution is boiled to remove nitrous acid and then titrated, first, with the stronger NaCl solution. When 100 Cc. of this solution have been added, the Ag present is nearly all precipitated and the titration is completed with the weaker NaCl solution, which is added in 0.5 Cc. portions, the titrated liquid being shaken between additions, until the V.S. ceases to produce a precipitate. The volumes of the two solutions used are then properly added and their sum accepted to represent a fineness of 1000, for convenience designated as " 1000 silver." To assay a sample of silver alloy, nearly the same quantity of silver (0.5 Gm.) must be taken for a titration. This is provided for by finding out the approximate amount of silver present in the sample by cupellation or by Volhard's titration of a separate portion and then employing that quantity of the alloy which will contain 0.5 Gm. of silver, or by making up the deficiency with the necessary quantity of pure silver. The sample is then dissolved and the solution titrated as in the standardization of the V.S. From the volume of NaCl V.S. consumed the fineness of the silver assayed is directly found.

18. Determination of Copper.

Cuprous thiocyanate is precipitated by a standard thiocyanate in excess and the unconsumed thiocyanate found by titration. Ag, Hg, halogens and cyanides must be absent.

Volumetric solutions employed: $\frac{N}{10}$ ammonium thiocyanate and $\frac{N}{10}$ silver nitrate.

Indicator: Ammonium ferric sulphate solution.

A suitable quantity for titration is 0.3 to 0.4 Gm. of crystalline $CuSO_4$. Dissolve the accurately weighed portion in 20 Cc. of water, neutralize with Na_2CO_3 solution, if necessary (though the solution may be weakly acid), add 10 Cc. of 6 per cent. sulphurous acid,

[1] See method of preparation, page 165.

heat to boiling and precipitate with $\frac{N}{10}$ ammonium thiocyanate V.S. Add the V.S. slowly to the hot liquid until the green precipitate, first produced, gives place to a white CuSCN or until an excess of the V.S. has been added. Confirm this by removing a drop of the clear supernatant liquid and add to it, in a test tube, a few drops of the thiocyanate and, if necessary, add more of the V.S., returning the test portion. When the precipitation is completed, transfer the mixture to a 500-Cc. measuring flask, dilute it to 300 or 400 Cc. with distilled water, let stand 15 minutes, and add water to make it measure exactly 500 Cc. Filter through a dry paper, reject the first portion of the filtrate and titrate the remainder in aliquot portions (100 Cc.). To each such portion add $\frac{N}{10}$ silver nitrate V.S. in excess, acidify with HNO_3, introduce the indicator and titrate with the $\frac{N}{10}$ thiocyanate V.S. so that finally one drop of the V.S. shall produce a distinct reddish color. From the volume of $\frac{N}{10}$ thiocyanate V.S. consumed by the sample, calculate the percentage of the copper salt or of Cu present. The principal reaction is represented:

$$\underset{2 \times 249.74}{2CuSO_4 \cdot 5H_2O} + \underset{2 \times 76.13}{2NH_4SCN} + SO_2$$

$$= 2CuSCN + (NH_4)_2SO_4 + 2H_2SO_4 + 3H_2O.$$
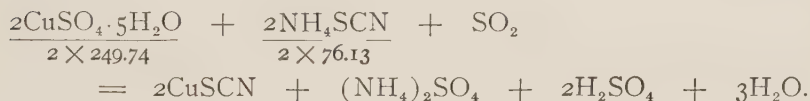
76.13 parts of NH_4SCN react with 249.734 parts of crystalline $CuSO_4$ containing 63.57 parts of Cu.

1 Lt. of $\frac{N}{10}$ NH_4SCN contains 7.614 Gm., and corresponds to 24.974 Gm. of $CuSO_4 \cdot 5H_2O$.

1 Cc. of the V.S. is the equivalent of 0.024974 Gm. of crystalline copper sulphate, or of 0.006357 Gm. of metallic copper.

Observations.—Should a black precipitate be produced on addition of the $\frac{N}{10}$ thiocyanate V.S., an insufficient amount of SO_2 is indicated. Halogens, in a sample to be titrated, are removed by repeated evaporation with HNO_3. Nitric acid dissolves CuSCN giving low results; the acid should be neutralized. To remove Ag, Pb, Hg or Sb when present, the solution in nitric acid of a portion to be taken for titration is evaporated with a little sulphuric acid until white fumes of SO_3 are given off, the residue taken up with water or with dilute HCl when silver is present, the mixture filtered and the precipitate washed free from copper. In the filtrate and washings combined, the copper is titrated as given above.

19. DETERMINATION OF BISMUTH. I. (Method of Frerich.)

Freshly precipitated Bi_2S_3 reacts quantitatively with $AgNO_3$. An excess of standard silver nitrate is added and the excess titrated by Volhard's method.

The bismuth in a solution of the portion taken for analysis, is precipitated by H_2S, the precipitate washed with H_2S water at first, then with water to completely remove H_2S and chlorides. The washed precipitate is transferred to a graduated, glass-stoppered 100 Cc. cylinder, for each 0.1 Gm. of Bi, 25 Cc. of accurately meas-

ured $\frac{N}{10}$ silver nitrate are added and the contents shaken vigorously
during one half hour.   The mixture is then diluted to any definite
volume (100 Cc.), allowed to deposit the precipitate of Ag_2S and
aliquot portions of the clear liquid are titrated with $\frac{N}{10}$ thiocyanate
V.S. in the presence of ammonium ferric sulphate as indicator.

1 Cc. of $\frac{N}{10}$ $AgNO_3$ is the equivalent of 0.006933 Gm. of bismuth,
or of 0.007733 Gm. of bismuth oxide.

20. Determination of Formaldehyde.   (The Cyanide Method.)

Formaldehyde forms, with KCN, a soluble compound which in
acid solutions does not react with silver nitrate.   The formalde-
hyde to be determined is made to react with an excess of standard
KCN and the excess of the reagent titrated.

Volumetric solutions employed: $\frac{N}{10}$ silver nitrate, $\frac{N}{10}$ thiocyanate
and empirical potassium cyanide.   The exact relation between the
cyanide and $\frac{N}{10}$ $AgNO_3$ V.S. is established by titration at the time of
the determination.

Indicator: Ammonium ferric sulphate solution.

To 15 or 20 Cc. of $\frac{N}{10}$ $AgNO_3$ V.S., accurately measured into a
100-Cc. flask, are added 10 drops of 50 per cent. nitric acid, and 10
Cc. of the empirical KCN V.S. run in from a burette.   The mixture
is diluted to 100 Cc. with water, shaken well and filtered through a
dry filter, the first portion which passes through being rejected.   Of
the filtrate, 50 Cc. are titrated with $\frac{N}{10}$ ammonium thiocyanate V.S.
in the presence of 5 Cc. of ammonium ferric sulphate solution as
indicator.   This gives the ratio of KCN solution to the $\frac{N}{10}$
$AgNO_3$ V.S.

To assay a sample of formaldehyde solution, 30 to 40 Cc. of the
KCN V.S. are accurately measured into a flask and to it are added
10 Cc. of the sample solution containing about 0.2 Gm. of a 40
per cent. solution of formaldehyde, then an excess (10 to 20 Cc.)
of $\frac{N}{10}$ silver nitrate V.S., the mixture acidified with HNO_3 and
diluted to 100 Cc.   After thorough shaking the mixture is filtered
through a dry filter, the first portion of the filtrate being rejected.   In
50 Cc. of the filtrate the excess of $AgNO_3$ is determined by titration,
with $\frac{N}{10}$ thiocyanate V.S., using ammonium ferric alum solution as
indicator.

From the volume of standard potassium cyanide V.S. consumed
by the formaldehyde, the percentage of the latter, present in the
sample, is calculated.

$$\underset{30.02}{\underline{HCOH}} + KCN = KOCH_2CN.$$

$$AgNO_3 + KCN = AgCN + KNO_3.$$

$$AgNO_3 + NH_4SCN = AgSCN + NH_4NO_3.$$
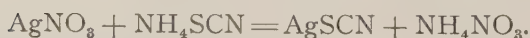
1 Cc. of $\frac{N}{10}$ V.S. is the equivalent of 0.003002 Gm. of HCOH.

For calculation of results, the volume of a tenth-normal V.S.
which is the equivalent of the Cc. of the empirical KCN V.S. may

be found, or the value of one Cc. of the solution calculated and employed as the factor. Acetaldehyde, if present, will give higher results, especially if the mixture be allowed to stand some time; hence the titration should be performed with expedition. Acetone and benzaldehyde, when present, do not affect the results. The method gives good results with very weak solutions of formaldehyde.

21. DETERMINATION OF BISMUTH. II. (Rupp and Schaumann.)

Bismuth dichromate is precipitated by an excess of standard potassium chromate, and the excess of the reagent titrated iodometrically.

Volumetric solutions employed: Standard potassium chromate and $\frac{N}{10}$ sodium thiosulphate. The standard potassium chromate may be prepared by dissolving the required quantity of pure K_2CrO_4 in water, or is conveniently obtained by adding to a strong solution of $K_2Cr_2O_7$ a solution of KOH until red with phenolphthalein and discharging the red color with dilute acetic acid, then diluting to a definite volume. In either case the V.S. should be standardized with the thiosulphate.

To 30 Cc. of the standard chromate contained in a flask, add the solution of the Bi salt which should contain the least quantity of free acid and not more than 0.1 Gm. of Bi, dilute to 100 or 200, mix well by shaking during 10 minutes and filter through a dry filter, rejecting the first portion that passes through. The filtrate, which should be tested for the absence of Bi with a few drops of ammonium hydroxide is then titrated in 20 Cc. portions, adding to each, 1 Gm. of KI and 10 Cc. sulphuric acid $(1 + 5)$. Let stand 5 minutes, dilute with an equal volume of water and titrate with the $\frac{N}{10}$ thiosulphate with 1 Cc. of starch solution, added when the color of the titrated liquid becomes yellow. One drop of the V.S. should finally discharge the blue color. From the volume of standard chromate consumed by Bi, calculate the percentage of the metal in sample. The reactions involved are represented:

$$\underset{2 \times 208(Bi)}{2Bi(NO_3)_3} + \underset{294.4(K_2Cr_2O_7)}{2K_2CrO_4} + H_2O$$
$$= (BiO)_2Cr_2O_7 + 4KNO_3 + 2HNO_3.$$

$$2K_2CrO_4 + 6KI + 8H_2SO_4$$
$$= 6I + 5K_2SO_4 + Cr_2(SO_4)_3 + 8H_2O.$$

$$6I + \underset{6 \times 248.24}{6Na_2S_2O_3 \cdot 5H_2O} = \text{etc.}$$
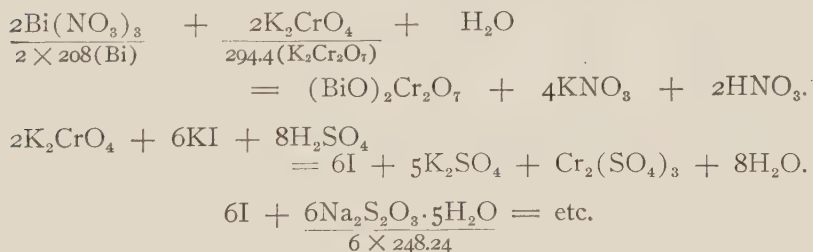
2×208 Gm. of Bi, in bismuth salt, react with 294.4 parts of $K_2Cr_2O_7$ as $2K_2CrO_4$. This quantity of the dichromate liberates 6×126.92 parts of iodine which require 6×248.24 parts of sodium thiosulphate for combination; the relation among these substances being:

$$208\,Bi = \frac{294.4}{2}\,K_2Cr_2O_7 = 3 \times 126.92\,I = 3 \times 248.24\,Na_2S_2O_3 \cdot 5H_2O.$$

1 Lt. of $\frac{N}{10}$ $K_2Cr_2O_7$ contains 4.9066 + Gm., and corresponds to 6.933 + Gm. of Bi.

1 Cc. of the V.S. is the equivalent of 0.006933 + Gm. of metallic bismuth.

Observations.—It is evident that an excess of $\frac{N}{10}$ chromate V.S. must be employed, and this must be at least twice the volume needed to precipitate all the Bi present. While HNO_3, which has a solvent action on bismuth dichromate and would liberate iodine if uncombined, is produced in the reaction, it becomes harmless through its reaction with the excess of the chromate as follows:

$$K_2CrO_4 + 2HNO_3 = K_2Cr_2O_7 + 2KNO_3.$$

This also explains why the dichromate can not be used for precipitation. Neutralization of the free acid in the Bi salt solution or that formed in reaction with an alkali or an acetate is not to be practiced.

For accurate results the $\frac{N}{10}$ potassium chromate should be standardized with a standard solution of pure bismuth nitrate, the standardization being made under the conditions of the determination. The measuring vessels should be in perfect agreement and measurings carefully performed.

Though many other methods have been proposed and recommended for the determination of Bi volumetrically, they are all more or less difficult of execution and are not free from the incubus of all volumetric methods for bismuth which arises from the tendency of this element to form basic compounds of variable composition. Small quantities of Bi may be determined colorimetrically.

22. DETERMINATION OF ZINC.

Volumetric solution employed: Standard potassium ferrocyanide V.S.

Indicator: Uranium acetate solution.

Accurately weigh of a salt or employ of a solution such quantity as to contain 0.1–0.5 Gm. of zinc. Dissolve, acidify the solution, oxidize Fe with Br and remove it by precipitation with ammonium hydroxide (see standard ferrocyanide V.S.), or, by boiling the solution, just acidified with HCl, with aluminium foil during 3 minutes. The foil is then removed. Al removes Fe, Pb, Cu and Cd by precipitation, while its salts have no effect on K_4FeCN_6. Add to the solution, free from the interfering metals, some NH_4Cl (1 Gm.), acidify with HCl, if necessary, dilute to 150 Cc. and titrate with the standard ferrocyanide V.S. in the manner in which the V.S. was standardized. From the volume of standard potassium ferrocyanide consumed in this and another titration, the percentage of zinc present is readily calculated by employing the nearest factor found in the standardization of the V.S., q. v.

Observations.—Ammonium chloride helps to settle the precipitate and makes the end-reaction sharper. Hydrochloric acid, which also helps to produce a sharp end-reaction should not exceed 10 Cc. concentrated acid per 150 Cc. of a solution containing 0.2 Gm. zinc. Manganese is removed by Br water, or by H_2O_2. Nitrates and chlorates, in small quantities, do not interfere. Traces of Br. or NO_2 which act on K_4FeCN_6 are destroyed by Na_2SO_3; 2 drops of its 10 per cent, freshly made solution will be found sufficient to remove these and reduce any ferricyanide formed. Titration should begin at nearly 80° C. and be finished at about 40° C. With the increasing quantities of Zn the value of the factors will be found increased. For example, 20 Cc. Zn solution gives 0.005152; 50 Cc.=0.005195; 70 Cc. = 0.005206 and 100 Cc. = 0.005233 Gm.

Calcium chloride, sodium citrate and acids disturb the end-reaction through their solvent action on uranium ferrocyanide.

Nickel can be titrated with standard potassium ferrocyanide V.S. and $UO_2(C_2H_3O_2)_2$ indicator, in the manner given for determination of zinc. The solution to be titrated should contain a small but constant quantity of acetic acid. In applying the drop end-reaction test it is suggested to transfer a little of the liquid to two thicknesses of filter paper, adding the indicator to the lower one. This first serves to filter out any precipitate in suspension which would interfere in the reaction. Iron and other metals must of course be absent.

23. DETERMINATION OF THE SOLUBLE SULPHATES.

Sulphates are precipitated with standard $BaCl_2$ in excess and the excess titrated with standard chromate V.S.

Volumetric solutions employed: $\frac{N}{10}$ chromate and standard $BaCl_2$. The $\frac{N}{10}$ chromate is made by dissolving 7.363 Gm. of pure potassium dichromate in water, adding ammonium hydroxide to weakly alkaline reaction, and diluting to 1000 Cc. at standard temperature. The $BaCl_2$ solution should contain about 12.20 Gm. of the crystalline salt in 1000 Cc. and should be standardized with the $\frac{N}{10}$ chromate.

For the determination, a suitable quantity of the sample is dissolved in water, the solution heated, neutralized, if necessary, and the standard $BaCl_2$ run in slowly from a burette until an excess has been added. The mixture is then heated to boiling and the excess of the $BaCl_2$ titrated with the $\frac{N}{10}$ chromate V.S. The addition of the standard chromate should be made in 0.5 Cc. portions until, after mixing, the supernatant liquid is yellow colored. This color should be discharged by 0.2 to 0.4 Cc. of the standard $BaCl_2$. From the volume of the standard $BaCl_2$ solution consumed by the sample, the percentage of the particular sulphate is calculated. To represent the reactions:

$$Na_2SO_4 \;+\; BaCl_2 \;=\; BaSO_4 \;+\; 2NaCl.$$
$$142.7$$

$$2BaCl_2 + K_2Cr_2O_7 + 2NH_4OH = 2BaCrO_4 + 2KCl + 2NH_4Cl.$$
$$294.4$$
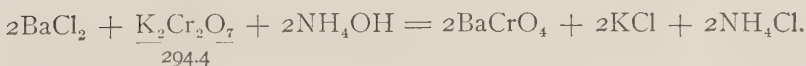
Note.—Other acids which precipitate barium must be absent. Carbonates are removed by heating with dilute acid and neutralizing before the addition of standard $BaCl_2$. If only a small quantity of a carbonate is present or the sample contains dissolved CO_2, the addition of a few drops of $CaCl_2$ solution will separate the CO_2. When the sample contains Mg, Zn or Cd some ammonium chloride should be added before titration.

Sulphuric acid and the soluble sulphates may be also determined with a solution of $BaCrO_4$ in HCl. In the reaction with a sulphate, barium sulphate and an equivalent quantity of a soluble chromate are formed; the chromate is then determined iodometrically.

According to T. Cooksey (J. Proc. Roy. Soc., N. S. W., 1907, 41–216), sulphuric acid is titrated with $BaCl_2$ and Na_2CO_3 V.S. The standard $BaCl_2$ V.S. is added in excess, the mixture stirred with alcohol and the excess of $BaCl_2$ titrated with standard Na_2CO_3 V.S. From the volume of standard barium chloride V.S. consumed by the acid the percentage of SO_3 is calculated.

24. Determination of Phosphoric Acid and the Soluble Phosphates.

Volumetric solution employed: Empirical uranium acetate.
Indicator: Potassium ferrocyanide solution.

Dissolve a suitable quantity of the sample (to consume from 20 to 30 Cc. of the V.S.), neutralize with NH_4OH, dissolve any precipitate formed in acetic acid, add 10 Cc. of an alkali acetate solution, acidify with acetic acid, if necessary, and heat to boiling. Titrate the hot solution with the standard uranium acetate V.S. in the manner in which the solution is standardized, page 169, titrating to the same shade of reddish-brown color accepted as the end-point in the standardization. From the volume of the V.S. consumed and obtained as an average of two or more agreeing titrations, calculate the percentage of the phosphate present. The result is commonly expressed in terms of P_2O_5. For calculation:

$$\frac{\text{Cc. of V.S. consumed} \times \text{equiv. of 1 Cc.} \times 100}{\text{Weight of sample}} = \text{per cent. of } P_2O_5.$$

Note.—Iron and aluminium, when present, interfere. Their phosphates, being insoluble in acetic acid, separate from solutions acidified with acetic acid; these metals must, on this account, be removed. If the quantity of the precipitate of Fe and Al phosphates is small, 1 per cent. or less, the washed precipitate may be ignited and one half of its weight considered as P_2O_5; when a large amount is found, the precipitate is dissolved in nitric acid and the phosphoric acid contained in it determined gravimetrically.

Soluble arsenates are titrated like the phosphates. Arsenous acid and its salts must, of course, be oxidized before titration.

Phosphates may also be determined by precipitation as ammonium phospho-molybdate in acid solution. The yellow precipitate is washed, dissolved in standard alkali in excess and the excess titrated

with standard sulphuric acid, using phenolphthalein (Pemberton's method). Since the composition of the yellow precipitate has been found to vary with concentrations of the solution of a sample, as well as of the reagents used, and the duration of heating, etc., it is essential that titrations be made under fixed conditions. Sulphates in the sample are objectionable and should be removed by $BaCl_2$ solution.

SUGARS.

25. Determination of Reducing Sugars.

Glucose (dextrose, levulose), invert sugar, milk sugar and maltose. Volumetric solution employed: Standard alkaline cupric tartrate.

Into a 50 Cc. erlenmeyer flask measure exactly 10 Cc. of the Fehling solution, add 10 Cc. of distilled water, heat rapidly to boiling and titrate the hot solution, which should be perfectly clear, with a solution of the sample. The sample solution, 0.5 to 1 per cent. (its exact strength must be known), is run in from a burette in small portions, the mixture quickly brought to boil after each addition, until all copper is precipitated as cuprous oxide, at which point boiling is kept up for 2 minutes longer. The end-point of the reaction becomes known by the disappearance of the blue color of the solution; the absence of copper in the titrated liquid may, however, be ascertained by testing drop portions of it, removed to a clean watch glass and acidified with acetic acid, with a drop of potassium ferrocyanide solution. The absence of Cu is indicated by the nonproduction of a brown color. The first titration should serve as a trial test to show, approximately, the volume of a sugar solution required to reduce a definite volume of the V.S. In the subsequent titrations nearly all of this volume of the sample is run into the hot Fehling solution at once, the mixture boiled 2 minutes, and the titration completed with 0.2 Cc. portions of the sugar solution. From the volume of the solution of the sample consumed in the titration, the quantity of reducing sugar is easily found and the percentage of sugar in sample calculated. If, for example, the solution of the sample contained 0.564 Gm. of the sample in 100 Cc. and 9.5 Cc. of the solution were consumed to reduce 10 Cc. of the Fehling solution, then, since 10 Cc. of the V.S. correspond to 0.05 Gm. of glucose, it is evident that the titration indicates that much glucose in 9.5 Cc. of the sample solution. As these 9.5 Cc. of the solution were made to contain 0.051258 Gm. of the sample, the percentage of glucose in the sample is:

$$0.05125 : 0.05 :: 100 : x.$$

$$x = 97.54 \text{ per cent.}$$

Observations.—The number of reboilings should be as small as possible; lactose requires 6 minutes boiling. Substances which reduce Fehling solution on heating, such as chloroform, phenyl hydrazine, uric acid, creatinine, salicylic acid, etc., must not be

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present in the solution of the sample.   Dark-colored solutions (some urines) are often decolorized, previous to titration, with milk of lime, suspended aluminium hydroxide or basic lead acetate. When lead subacetate is used it is important to remove all lead from the solution, best with Na_2CO_3.   It has been observed (Soxhlet) that the reducing power of glucose is influenced by the concentration of the solutions used in determinations.   Thus if, at any time, more copper salt is present than the sugar can reduce, its reducing power is increased, and conversely, by adding the sugar to the copper solution in a number of successive portions, the reduction of copper becomes a decreasing quantity.   Therefore, the factor for glucose with Fehling solution can not be generally accepted as true, being so only for a certain set of conditions.   As a rule the V.S. should be standardized with a pure sample of that sugar which is to be determined, and the titration for standardization exactly duplicated in the determination.

Levulose is decomposed when heated with alkalies.   Solutions of sugar for titration of the Fehling solution should be about 0.2 per cent. strong.   1 Gm. of pure glucose corresponds from 195 to 205 Cc. of the alkaline Cu tartrate V.S.

An indicator has been recommended for use in this titration. Its composition is: ammonium thiocyanate 1.5, ferrous ammonium sulphate 1 Gm., HCl, U.S.P., 2.5 Cc., and water 10 Cc.   The solution is decolorized by the addition of zinc dust.   If need be, the addition is repeated, though too often decolorization decreases the sensitiveness of the indicator.   The drop end-point method is used and the test is made by bringing a drop of the titrated liquid into the middle of a drop of the indicator on a white plate.   Red-brown color indicates the presence of copper and no brown color, finally, the end-reaction.

To overcome the disturbing influence of the precipitated Cu_2O on the observation of the end-reaction, Gerard has modified the method of titration as follows: To 10 Cc. of the Fehling solution are carefully added portions of 5 per cent. KCN solution until it is just decolorized, the colorless liquid is mixed with exactly 10 Cc. of the Fehling solution and the warm mixture titrated with the sugar solution to decolorization.   The Cu_2O, otherwise separating, remains dissolved.   Calculation is based on 10 Cc. of the V.S.

10 Cc. of alkaline cupric tartrate V.S. require, for complete reduction to Cu_2O, 0.05 Gm. dextrose, 0.05 Gm. levulose, 0.05 Gm. invert sugar, 0.0475 Gm. cane sugar (inverted), 0.0806 Gm. maltose, 0.0678 Gm. milk sugar, 0.045 Gm. starch (hydrolyzed).

26. MALTOSE IN MALT-EXTRACT.

A solution of the sample, 0.1 per cent. strong, is prepared and employed for titration of 10 Cc. of the Fehling solution as described under glucose, see 25. $\dfrac{806}{\text{Cc. used}}$ = per cent. of maltose in the sample.

27. Determination of the Diastatic Value of Malt or Malt Extract.

Solution of potato starch is prepared in the usual manner. Of this solution a quantity, equal to 1 Gm of dry starch, is prepared by mixing 1 Gm. of pure starch with a few Cc. of cold distilled water and pouring the mixture into 65 Cc. of boiling water, the starch being completely washed out with small portions of cold water. The mixture is made to measure 80 Cc. and boiled 1 minute to complete the gelatinization of the starch. When the starch solution, thus obtained, has cooled to 40° C., 20 Cc. of 1 per cent. solution of the malt-extract are added, the mixture stirred and kept at 40° C. during one half hour. By heating then to 100° C. the action is interrupted and, on cooling, the solution is employed for titration of 10 Cc. of the alkaline copper tartrate V.S. See No. 25.

$\dfrac{806}{\text{Cc. used}} =$ per cent. of total maltose. By finding the percentage of preëxisting maltose and subtracting this from the total percentage found, the maltose produced by the diastase in one half hour, at 40° C., is obtained. Of this value $\dfrac{100}{84.4}$ is the quantity of converted starch.

28. Determination of Cane Sugar.

The nonreducing sugars become reducing by inversion. This is brought about by heating with a dilute acid. To invert a portion of a sample for titration 0.5 Gm. of it is dissolved in 50 Cc. of water, 5 Cc. of concentrated HCl added, and the solution gradually heated to 70° C., and maintained at this temperature during 5–8 minutes. After cooling, the solution is neutralized with NaOH or Na_2CO_3 solution, made up to a definite volume (100 Cc.) and employed for titration of 10 Cc. of the alkaline cupric tartrate V.S. as given under reducing-sugars.

1 Cc. of Fehling solution is the equivalent of 0.00475 Gm. sucrose.

29. Determination of Starch.

Starch is hydrolyzed by heating with an acid. This treatment is direct, or, when other copper-reducing substances are present in the sample, after digestion of the sample with diastase. In either case 2 Gm. of the sample are mixed with water and kept at the temperature of boiling water during 15 minutes, cooled, diluted to 200 Cc. and heated with 20 Cc. of HCl (1.125) under a return condenser (Fig. 29) during two and one half hours. The solution, on cooling, is neutralized with NaOH, made up to 250 Cc., filtered, if necessary, and used for titration as the glucose solution. When diastase is used to convert starch into reducing-sugars the quantity of reducing sugar in a volume of it, equal to that used for the starch, must be determined, this portion being subjected to the same treatment as that used for starch.

1 Cc. of Fehling solution is the equivalent of 0.0045 Gm. of starch. Starch in spices, etc., is hydrolyzed after a treatment with

diastase, the sample being extracted with ether or alcohol + ether previously.

30. DETERMINATION OF PHENOL.

Phenol reacts with standard bromine V.S. in excess and the unconsumed bromine is titrated.

Volumetric solutions employed: $\frac{N}{10}$ bromine and $\frac{N}{10}$ thiosulphate.

Dissolve 1 Gm. of the sample in enough water to measure, at standard temperature, 500 Cc.   Transfer exactly 20 Cc. of this solution containing 0.04 Gm. of sample to a 200-Cc., glass-stoppered bottle, add 35 Cc. of $\frac{N}{10}$ bromine V.S., measuring this accurately, then 5 Cc. of strong HCl, close the bottle and keep its contents agitated by shaking during one half hour.   Introduce 5 Cc. of 20 per cent., pure potassium iodide quickly and carefully so that no Br vapor escape, close at once and mix well by shaking.   Wash any iodine on stopper and neck of the bottle into the bottle with some cold water, add 1 Cc. of chloroform and shake well.   Titrate the iodine liberated in the mixture with $\frac{N}{10}$ thiosulphate V.S., added slowly, so that the final yellow color of the titrated liquid is just discharged by one drop of the V.S.   The volume of $\frac{N}{10}$ bromine consumed by phenol is obtained when the Cc. of the $\frac{N}{10}$ thiosulphate V.S. are subtracted from 35, the Cc. of $\frac{N}{10}$ bromine V.S. taken.   From the volume of the $\frac{N}{10}$ Br V.S. consumed, the percentage of phenol in sample is calculated.   The factor for phenol, with $\frac{N}{10}$ V.S. is 0.0015675 Gm., and is derived from the following equations:

$$5KBr + KBrO_3 + 6HCl = 6KCl + 6Br + 3H_2O.$$

$$\underset{94.06}{C_6H_5OH} + \underset{6 \times 79.92}{6Br} = C_6H_2Br_3OH + 3HBr.$$

$$2Br + 2KI = 2KBr + 2I \cdots 2I + 2Na_2S_2O_3 \cdot 5H_2O = \text{etc.}$$
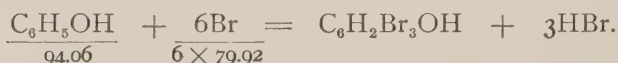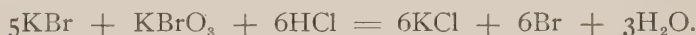
6×79.92 parts of bromine react with 94.06 parts of phenol. Since 1 Lt. of $\frac{N}{10}$ Br V.S. contains 7.992 Gm., and corresponds to 1.5675 Gm. of phenol,

1 Cc. of the V.S. is the equivalent of 0.0015675 Gm. of phenol.

To calculate:

$$\frac{\text{Cc. of } \frac{N}{10} \text{ Br consumed} \times 0.0015675 \times 100}{\text{Weight of sample}} = \text{per cent. of phenol.}$$

Observation.—Phenol with the bromine forms tribrom-phenol, each molecule of phenol consuming 6 Br, of which 3 substitute 3 hydrogens in the molecule, and the other 3 combine with the hydrogen to HBr.   The bromine in excess liberates an equivalent quantity of iodine which is determined by titration with $\frac{N}{10}$ thiosulphate V.S.   The KI used should be free from iodate, and the two V.S. should have been recently standardized.   Chloroform serves to dissolve the tribrom-phenol which precipitates.

TABLE OF EQUIVALENTS (*factors*).

1. Tenth-Normal Silver Nitrate V.S.

1 Cc. of $\frac{N}{10}$ silver nitrate V.S. contains 0.016989 Gm. of $AgNO_3$ and is the equivalent of:

	Gramme.
Allyl iso-thiocyanate, $C_3H_5 \cdot NSC$	0.0049565
Ammonium bromide, NH_4Br	0.009797
Ammonium chloride, NH_4Cl	0.005351
Ammonium iodide, NH_4I	0.014497
Ammonium thiocyanate, NH_4SCN	0.007613
Barium chloride, $BaCl_2 \cdot 2H_2O$	0.0122165
Barium chloride, anhydrous, $BaCl_2$	0.0104145
Bromine, Br	0.007992
Bromoform, $CHBr_3$	0.008426
Calcium bromide, $CaBr_2$	0.099965
Calcium chloride, $CaCl_2$	0.00555
Carbon tetrachloride, CCl_4	0.003848
Chloral hydrate, $CCl_3CHO + H_2O$	0.005513
Chlorine, Cl	0.003546
Chloroform, $CHCl_3$	0.003979
Cuprous thiocyanate, CuSCN	0.012165
Ferrous bromide, $FeBr_2$	0.0107845
Ferrous chloride, $FeCl_2$	0.0063385
Ferrous iodide, FeI_2	0.0154845
Hydriodic acid, HI	0.012793
Hydrobromic acid, HBr	0.008093
Hydrochloric acid, HCl	0.003647
Hydrocyanic acid, HCN (by Liebig's method)	0.005404
Hydrocyanic acid, HCN (by Mohr or Volhard method)	0.002702
Hydrogen sulphide, H_2S	0.0017045
Hydrothiocyanic acid, HSCN	0.005909
Iodine, I	0.012692
Iodoform, CHI_3	0.013126
Lithium bromide, LiBr	0.008692
Potassium bromate, $KBrO_3$	0.016702
Potassium bromide, KBr	0.011902
Potassium chlorate, $KClO_3$	0.012256
Potassium chloride, KCl	0.007456
Potassium cyanide, KCN (Liebig's method)	0.013022
Potassium iodate, KIO_3	0.021402
Potassium iodide, KI	0.016602
Potassium thiocyanate, KSCN	0.009718
Silver, Ag	0.010788
Silver oxide, Ag_2O	0.011588
Silver sulphate, Ag_2SO_4	0.015592
Sodium bromate, $NaBrO_3$	0.015092
Sodium bromide, NaBr	0.010292
Sodium chlorate, $NaClO_3$	0.010646
Sodium chloride, NaCl	0.005846
Sodium iodide, NaI	0.014992
Strontium bromide, anhydrous, $SrBr_2$	0.012373
Strontium bromide, $SrBr_2 + 6H_2O$	0.017779
Strontium iodide, $SrI_2 + 6H_2O$	0.022479
Zinc bromide, $ZnBr_2$	0.011277
Zinc chloride, $ZnCl_2$	0.006831
Zinc iodide, ZnI_2	0.015977

2. Tenth-Normal Thiocyanate V.S.

1 Cc. of $\frac{N}{10}$ thiocyanate V.S. contains 0.009718 Gm. of KSCN or 0.007613 Gm. of NH_4SCN and is the equivalent of:

Gramme.

Copper, Cu 0.006357
Copper sulphate, $CuSO_4 + 5H_2O$ 0.024974
Silver, Ag 0.010788
Silver nitrate, $AgNO_3$ 0.016989

3. Tenth-Normal Sodium Chloride V.S.

1 Cc. of $\frac{N}{10}$ sodium chloride V.S. contains 0.005846 Gm. of NaCl and is the equivalent of:

Gramme.

Silver, Ag 0.010788
Silver nitrate $AgNO_3$ 0.016989
Silver oxide, Ag_2O 0.011588

4. Standard Fehling's Solution.

1 Cc. of standard alkaline copper tartrate V.S. contains, approximately, 0.0088285 Gm. of copper and is the equivalent of:

Gramme.

Glucose (dextrose or levulose) 0.005
Invert sugar 0.005
Cane sugar (inverted) 0.00475
Milk sugar 0.00678
Malt sugar 0.00806
Starch (hydrolized) 0.0045

5. Tenth-Normal Bromine V.S.

1 Cc. $\frac{N}{10}$ bromine V.S. contains 0.007992 Gm. of Br and is the equivalent of:

Gramme.

Phenol, C_6H_5OH 0.0015675

CHAPTER V.

Determinations by Comparison of Colors.

Titrations, as has been pointed out, become less accurate the smaller the quantity of the substance treated, or the lower the percentage of the ingredient to be determined. This applies equally well to the gravimetric methods; the coefficient of error increasing as the quantities weighed become smaller within certain limits.

When the quantity of the substance to be determined falls within the limits of great inaccuracy which passes beyond the weighable amounts, other methods of determination must be resorted to.

By color comparison, or color matching, very small quantities of many substances can be determined with a satisfactory degree of accuracy. The comparison of colors, or correctly stated, the matching of the intensities of the same shade of color in two or more solutions, is naturally available only for substances possessing color or giving colored products with reagents.

The intensity of color of a solution depends on the concentration of the dissolved substance and may, therefore, be utilized for purposes of quantitative determinations. Determinations by comparison of the intensities of two colored solutions is known as *Colorimetry or Tintometry*. Just as in titrations, the quantity of the substance determined is calculated from the volume of a V.S. consumed by a given quantity of the sample, the amount of a substance determined colorimetrically is obtained from the quantity of a standard solution required to give a color of equal intensity when treated with the same reagents and under precisely analogous conditions. However, calculation of the results is in many cases based on the thickness of the liquid viewed. In two solutions of definite contraction, contained in vessels of the same size and shape, the quantities of the colored substances present are in inverse proportion to the thicknesses of the layers viewed.

In practice, color-matching is carried out by two distinct methods which give rise to the construction of colorimeters of two types. In one, equal volumes of two or more solutions are compared in vessels of the same size and shape so that the columns of the liquids observed are equal, the illumination being also equal and uniform. The adjustment of tints is brought about by dilution of the more intensely colored liquid or through varying the quantity of a standard solution used in the control test by repeated trials until the desired agreement is obtained. Calculation of the results is based on the quantity of the pure reagent or of a standard solution of it added to the control test.

The other method employs two solutions; one of the sample and the other of a standard reagent, the solutions being of definite concentrations. These solutions are compared in vessels of the same

dimensions, Fig. 34, and, if the intensity of their color is found to vary, the adjustment is made by changing the volumes exposed to view so as to make their colors appear alike.   Ordinarily the volume of the more intensely colored liquid is diminished by removing some of the solution; in some cases light is made to reach the eye through a thinner layer of the liquid.   Calculation is made from the thickness of the liquid viewed, the quantity of the substance present being inversely proportional to the thickness of the layer of the liquid exposed to view.

The comparison is commonly between a solution of a sample and that of a standard similarly treated, though permanent standard tints are also used.

When a reaction, on which color production depends, proceeds slowly or completes itself after a definite period of time (the color being then most intense) the observation of the two liquids must be made simultaneously and with special attention to the time set for observation.   To economize on time the first comparison may be used as a trial test and the more intensely colored liquid diluted

FIG. 34. HEHNER'S
CYLINDERS.

so as to find the approximate quantity of the standard reagent to be employed in the subsequent comparisons.

The solutions to be compared must be clear and must not be very intensely colored.   Turbidity, due to precipitation or to any other cause, has a very marked influence on color intensity comparisons and interferes with the determinations.   Intensely colored solutions, not permitting ready detection of

FIG. 35. A RACK OF COLOR TUBES.

changes in concentration, are unsuited for colorimetric determinations and should, therefore, be properly diluted or a smaller quantity of the sample treated.

To measure the relation of color intensity to the quantity of the substance dissolved, the color of a layer, 1 Mm. thick of a solution of 1 Gm. of iodine is 10,000 Cc. of water was proposed as the unit and called " colorie."

The vessels most commonly employed are tall cylinders known as " Nessler tubes," Fig. 36.   These should be made of clear, colorless glass, and those used in a determination should be of the same height and diameter; they are made of 50, 100 and 150 Cc. capacity. Test-tubes are not as suitable for this purpose though often em-

ployed.   The Nessler tubes are usually stood on a level surface or
set in specially constructed racks, Fig. 35.   An ordinary test-tube
rack with porcelain bottom carrying tall, 100 Cc. cylinders, as
devised by Proskauer, is admirably suited for most purposes.   Nes-
sler tubes are calibrated to
hold definite volumes and
can be used only for com-
parison of equal volumes
of two or more liquids.
For comparison of unequal
volumes, graduated cylin-
ders, usually with an outlet
near the bottom, are em-
ployed, Fig. 34.
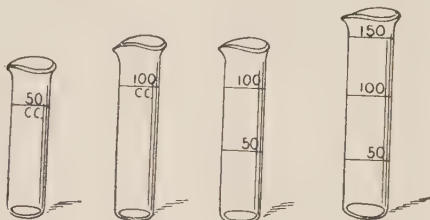
Fig. 36.   Nessler Tubes.

The liquids are usually viewed by looking through the uncovered
tubes, from the top, in good diffused daylight, best in a window
in which they are placed, against a white background.   In some
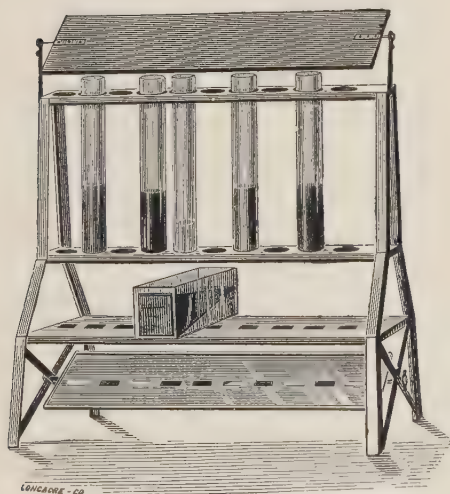
Fig. 37.   Leed's Color Comparator with Prism.   Fig. 38.   Dubosc Soleil's Colorimeter.
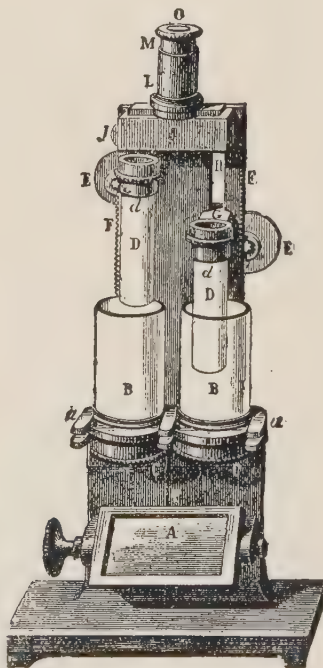
cases it is of advantage to wrap black paper around the sides of
the tubes or place them in a dark box in order to eliminate other
light than that which is desired to pass through them to illuminate
the liquid.   In the numerous and often elaborate colorimeters, the
tubes, or tanks, holding the liquids are observed in a camera in
which the light which illuminates the liquids passes only in one
direction, Fig. 38.

Color reactions are often modified through changes in temperature and the presence of other substances in solution. Any interfering agent should be carefully removed; if this is found impracticable, a quantity of it, equal to that present in the treated portion of the sample, should be added to the control test. It is, therefore, specially important to carry out a set of color reactions for comparison under as nearly identical conditions as it is possible to provide.

I. Ammonia and Ammonium Salts. (In Very Small Amounts.) (I.)

Ammonia and ammonium salts in solution react with alkaline mercuric-potassium iodide, producing a yellow-colored compound. From the intensity of the coloration when matched with a solution containing a known quantity of ammonia the amount of ammonia in sample is found.

Reagents:

1. *Standard Ammonium Salt Solution,* containing in 1 Cc. 0.01 Mgm. of NH_3. The solution may be prepared from pure $(NH_4)_2SO_4$, but is usually made by dissolving 1.5703 Gm. of pure, dry NH_4Cl in ammonia-free water to measure 500 Cc., and diluting exactly 5 Cc. of the solution to measure 500 Cc.

2. *Alkaline Mercuric-potassium Iodide Solution (Nessler's Reagent).*—To prepare this, a saturated solution of $HgCl_2$ (20 Gm.), in water, is poured in small portions into a solution of 20 Gm. of KI in 100 Cc. of water until, the mixture being well stirred, a permanent precipitate just forms. To this are added 80 Gm. potassium hydroxide, and, when dissolved, the solution diluted to measure 500 Cc. To the solution is finally added the saturated $HgCl_2$ solution in small portions, mixing until a red precipitate is formed; the mixture is allowed to stand and the clear, supernatant liquid drawn off when needed.

3. *Ammonia-free Water.*—Water is distilled with a little ignited sodium carbonate and, when the distillate gives no color with 2 Cc. of Nessler's solution, it is collected and kept well-stoppered for use.

Into one Nessler cylinder (tube) place 50 Cc. of the sample (in water analysis, 50 Cc. of the distillate), into another or several such, 50 Cc. of ammonia-free water. Add to each, 2 Cc. of Nessler's solution, and add to the control tubes 0.5, 1, 2, etc., Cc. of the standard NH_3 solution. Mix the contents of the tubes well, cover each with a watch glass to protect it from atmospheric ammonia and examine the colorations produced after 10 minutes' standing. View the liquids vertically against a white background, the tubes being placed in good diffused sunlight (in a window). If the color of one of the standard tests exactly matches that of the sample, they evidently contain equal quantities of NH_3; otherwise the tubes nearest in point of color intensity are separated and the stronger-colored liquid diluted, with ammonia-free water, to such an extent that when 50 Cc. of it are returned to the Nessler cylinder, the intensity of its color will equal that of the other tube. The quantity of ammonia

present in these 50 Cc. is then calculated. If possible, another comparison should be made, the quantity of the standard solution required being increased or diminished as indicated by previous trial.

It is important to compare only clear solutions; color comparison and, therefore, the accuracy of the determination being markedly affected by precipitates or turbidity. In the comparison of two liquids the exact shade of color and its intensity must be chiefly regarded with the aim of making them mutually equal.

The method is suitable for only small quantities of ammonia; if a *brown* color appears on addition of Nessler's solution, the sample must be properly diluted with ammonia-free water before it can be treated for determination. The primary amines of the fatty acid series also react with Nessler's solution and, if present, interfere with color comparison; they should, therefore, be absent. The presence of calcium and magnesium salts is also objectionable. Small quantities of these salts present are removed by the addition of 2 Cc. of an alkaline sodium carbonate solution (10 per cent. each of $Na_2CO_3 + NaOH$), shaking thoroughly, allowing to settle, and drawing off portions of the clear liquid for nesslerization. Larger amounts of magnesium require the addition of $BaCl_2$ solution before the alkaline sodium carbonate is introduced.

2. AMMONIA AND AMMONIUM SALTS.
(TRILLAT AND TURCHET.) (II.)

Nascent iodine, acting on ammonia or ammonium salts in solution, produces a black-colored nitrogen iodide which serves for comparison.

Reagents:

1. *Standard Ammonium Chloride or Sulphate Solution* (see above).

2. *Sodium or Potassium Hypochlorite Solution* (2.5 per cent. of available Cl).

3. *Potassium Iodide*, 10 per cent. solution.

4. *Ammonia-free Water.*

Of a weak solution of ammonium salt, or of the distillate, 30 Cc. are measured into one Nessler cylinder, into the other is placed 1 Cc. standard NH_3 solution, and 30 Cc. of ammonia-free water. Then 10 drops of the KI solution, and 2 drops of the hypochlorite are added to each and the contents diluted to 50 Cc. If iodine color is prominent some more hypochlorite may be very cautiously added, or, what is to be preferred, any free iodine can be dissolved out by shaking with a little chloroform, which does not dissolve the nitrogen iodide. An excess of either KI or hypobromite must be carefully avoided. The comparison is made as in nesslerizing, the results being checked by another trial in which the required standard ammonium solution is properly adjusted.

If less than 2 Mgm. per 1000 Cc. of NH_3 are present the solution should be evaporated with a little dilute H_2SO_4 to a small volume,

the acid carefully neutralized with a carbonate and the liquid employed for treatment.

Note.—The advantages claimed for this method are: amino compounds, pyridine bases, nitrates, nitrites and albuminoid substances do not react and, therefore, are without influence when present; the method may be carried out directly with solutions and may be employed in case of cyanide or sulphate of ammonium.

3. Nitrites.   (Small Quantities as in Water.)

When a nitrite, naphthylamine and sulphanilic acid are brought together in acid solution, a red-colored azobenzol-naphthylamine sulphonic acid is formed.   The reaction is exceedingly delicate; the coloration is most intense in one half hour.

Reagents:

1. *Standard Nitrite Solution.*—The solution is prepared to contain 0.0001 Mgm. of N as nitrite in 1 Cc.   Of pure, dry silver nitrite 0.22 Gm. are accurately weighed and dissolved in hot water, NaCl is added in slight excess, the mixture cooled and diluted to measure 1000 Cc.   When clear, 5 Cc. of the supernatant liquid are removed by means of a pipette and diluted with distilled water to measure 1000 Cc.

2. *Sulphanilic Acid Solution.*—The solution is made 1 per cent. strong by heating with water and a little acetic acid.

3. *Naphthylamine Hydrochloride Solution.*—A sufficient quantity of the hydrochloride is boiled with water, during 10 minutes, to obtain a 0.5 per cent. solution, the volume of the boiling liquid being kept constant.   The solution is pinkish in color.

Unless the water is known to contain nitrites, it is tested as follows: In a Nessler tube, 100 Cc. of the sample are acidified with 3–4 drops of 10 per cent. HCl, 2 Cc. of sulphanilic acid solution added, then 2 Cc. of the naphthylamine solution introduced and the contents, after mixing with a glass rod, are covered with a glass plate and allowed to stand one half hour.   If a distinct red color develops within this time the nitrites are to be determined; a pinkish color is reported as "traces."   The intensity of the coloration will serve as an indication of the volume of the standard nitrite solution to be used in the control test.

To determine the nitrites another 100 Cc. or less, if the color was found too intense for comparison, are treated as in the trial test while a definite quantity of the standard nitrite solution, diluted with distilled water to the volume of the sample taken, is treated in another tube; the two tubes are allowed to stand covered during the same one half hour.   This is essential since the red color will begin to fade after 30 minutes.   As the air in the neighborhood of burning gas contains nitrous acid, protection for the solutions tested is necessary and is made by covering the tubes, or by their removal from the room.

The results are, in the case of water, expressed as nitrogen, parts per million.

4. NITRATES.   (SMALL QUANTITIES AS IN WATER.)   (I.)

Nitric acid combines with phenol in the presence of sulphuric acid to form picric acid of a yellow color. The color of ammonium picrate being even more intense, this salt is then formed and comparison of its color with a standard nitrate solution, also converted into picrate, is made.

Reagents:

1. *Standard Nitrate Solution.* (*W. P. Mason.*)—Of pure KNO_3, 0.7221 Gm. are dissolved to measure 100 Cc. Ten (10) Cc. of the solution are evaporated to dryness on water-bath, the residue moistened completely with 2 Cc. of phenol-disulphonic acid and the contents washed out into a liter flask and diluted to measure 1000 Cc. One (1) Cc. corresponds to 0.001 Mgm. of N as nitrate.

2. *Phenoldisulphonic Acid.*—Pure phenol, 30 Gm., and pure concentrated sulphuric acid, 370 Gm., are heated in a flask placed in boiling water during 6 hours.

3. *Standard Sodium Chloride Solution, 1.65 per thousand.*— Each Cc. corresponds to 1 Mgm. of chlorine.

To the residue of 20 or 100 Cc. of a sample of water, evaporated with 2 drops of a saturated solution of Na_2CO_3 on water-bath to dryness, are added 2 Cc. of the phenoldisulphonic acid, the dish is rotated so as to moisten the entire residue, few Cc. of water and enough 10 per cent. ammonium hydroxide is added to make the solution alkaline. The solution is then transferred to a Nessler tube, diluted to 100 Cc. and compared with a definite volume of the standard nitrate. The volume of this, required to match the color of the sample, is measured into another Nessler tube, made alkaline with 5 Cc. of NH_4OH solution, and diluted to 100 Cc. with distilled water. The solution which is the more intensely colored is then diluted to make the colors correspond. The results obtained are confirmed by another comparison in which the quantity of standard potassium nitrate used is properly adjusted.

When the proportion of chlorides, in water, is above 10 parts per million, they influence the reaction of nitrates to an appreciable extent and it becomes necessary to add to the standard test as much of the standard NaCl solution as will furnish an equal quantity of chlorine found in the volume of sample treated. To diminish the necessary errors of this determination, W. L. Dubois (J. A. Chem. Soc., 1906, 28, 1616), proposes the following modification: After heating the residue with phenoldisulphonic acid on a water-bath for one half hour, it is dissolved in water, washed into a flask, and the contents titrated with standard titanium chloride V.S., 1 Cc. of which $= 0.0005$ Gm. of KNO_3.

Results are expressed as nitrogen, parts per million.

5. NITRATE (NITRITE) IN WATER (BRUCINE METHOD).[1]   (II.)

Reagents:

Standard Solution of KNO_3 containing the exact quantity, per liter, of the pure KNO_3 which corresponds to 0.1 Gm. of HNO_3.

[1] H. Noll, Ztsch. ang. Chem., 14, 1317.

Solution of Brucine, 0.05 Gm. in 20 Cc. H_2SO_4, freshly prepared. A sample of water or a solution of nitrate must not contain more than 0.05 Gm. HNO_3 per liter; if stronger it should be diluted with distilled water.

Of the sample 10 Cc. are mixed with 20 Cc. of brucine solution during 15 minutes and poured into 70 Cc. of water in a Hehner cylinder. The color produced is matched with 5 Cc. of standard nitrate mixed with 5 Cc. of water and 20 Cc. of brucine solution during 15 minutes, and poured into 70 Cc. of water in another cylinder. The trials are repeated with varying quantities of the standard solution until the two tints are equal. Reaction must be brought about under the same conditions of time and temperature, the quantities given being adhered to. From the volume of standard KNO_3 required the amount of nitrate in sample is obtained. Nitrite acts like nitrate and is included.

6. Iron in Ferric Compounds.

Standard Iron Solution.—A solution of pure ferric chloride containing HCl is made preferably as follows: 10 Cc. of solution of ferric chloride (10 per cent. of Fe), strongly acid with HCl, are shaken out with ether, the ethereal solution allowed to evaporate spontaneously, the residue taken up with 10 Cc. of 10 per cent. hydrochloric acid and diluted with distilled water to measure 500 Cc. Fifty (50) Cc. of this solution are carefully measured into a beaker containing 5 Cc. of 10 per cent. NH_4OH, diluted with 100 Cc. of distilled water, and, if the mixture is not alkaline, NH_4OH is added to alkaline reaction. The contents of the beaker are heated to boiling and filtered through a quantitative filter paper. The precipitate is washed free from chlorides, dried, and ignited in a tared crucible to constant weight. The weight of ash of the filter paper is allowed for and from the weight of Fe_2O_3 obtained, the quantity of Fe in 50 Cc. is calculated:

$$\frac{Fe_2O_3}{159.7} : \frac{Fe_2}{111.7} :: \text{weight of precipitate} : x.$$

The remaining solution is then diluted so that 1 Cc. of it will contain 0.01 Mgm. of iron as $FeCl_3$.

(*a*) *With Ammonium Thiocyanate Solution.*
(For very small amounts of Fe.)

A definite quantity of the sample, containing a minute quantity of iron is acidified with 10 per cent. HCl, an excess of NH_4SCN solution (2 per cent.) added and the solution extracted with a mixture of amyl alcohol, 5 volumes, and ether 2 volumes. The extracted portion is then transferred to a tube for comparison with another obtained from a known quantity of the standard iron solution treated in the same manner. The solution which is more intensely colored is diluted with some of the solvent until the colors match. The quantity of iron in the control solution indicates the

amount of iron in sample. The mixture of ether and amyl alcohol may be replaced by acetone. Water to be treated for iron is evaporated (100 Cc.) with nitric acid (5 Cc.) to dryness, the residue ignited just to char the organic matter, then taken up with 5 Cc. HCl (1 + 1), the solution filtered, the filter washed. To the filtrate and washings 0.5 per cent. solution of potassium permanganate is added to the production of a pink color, lasting 5 minutes. Ammonium thiocyanate solution is then added in excess and the extraction and comparison with standard solution made.

(b) *With Potassium Ferrocyanide Solution.* (Fe in water.)

The water (100 Cc.) is evaporated to dryness in a platinum dish, the residue ignited to destroy organic matter, 1 Cc. of NH_4OH solution (1 part of stronger ammonia water in 20 parts of water) added, the mixture evaporated to dryness on a water-bath. The residue is dissolved in 1 Cc. of 10 per cent. HCl, 5 to 10 Cc. distilled water added, and the solution filtered into a Nessler cylinder. Potassium ferrocyanide solution, 5 per cent., is added (1 Cc.), and the coloration produced on mixing compared with one obtained by treating, with a standard iron solution, 1 Cc. of the ferrocyanide diluted to equal the volume of the sample in another Nessler tube. The standard Fe solution should be run in from a burette.

(c) *With Salicylic Acid.*

To a definite quantity of the sample, containing iron in solution as ferric chloride, is added an excess of 0.1 per cent. of salicylic acid solution in alcohol, and the mixture diluted to measure 50 or 100 Cc. in a Nessler cylinder. In another Nessler tube is similarly treated a definite volume of the standard iron solution, and the coloration produced in either case compared with the other. The solution which is the more intensely colored is diluted, with distilled water, to make its color correspond to the other, or the standard iron solution can be run into the control test, from a burette, until the desired color is produced. In either case the result should be confirmed by another comparison in which the required volume of standard iron solution is properly adjusted.

It has been observed that the depth of color and consequently the sensitiveness of the reaction may be increased by dissolving the salicylic acid in acetic acid with a small quantity of an acetate, preferably sodium acetate, added.

Zinc and antimony do not interfere when present. Lead is removed as $PbSO_4$ and copper, if present, is made colorless by the addition of dilute KCN solution.

(d) *With H_2S in Alkaline Solution.*

Very small quantities of inorganic iron salts in solutions containing an excess of pure alkali (best NH_4OH) give, with H_2S, a green color. The coloration is even more intense with organic salts or in the presence of organic compounds, so that albumin (4–5 Mgm.), added to a solution of an inorganic iron salt, helps to develop the

green color. The green color produced is regarded to be due to the presence of colloidal iron.

The quantity of ammonium hydroxide best adapted is 3 Cc. of a 6.2 per cent. solution for 50 Cc. of the liquid treated; into the alkaline liquid H_2S is passed during 10–12 minutes. With concentrations of 1–1,000,000, the addition of an equal volume of 90 per cent. alcohol should be made and the mixture allowed to stand 12 hours. Copper interferes and, if present, must be first removed by H_2S from an acid solution. Acids and oxidizing agents destroy the coloration. Other metals: Hg, Pb, Ag, Cr, Ni, Co and the alkaline-earths do not give the color.

Comparison is made with a small quantity of standard iron solution treated as the sample, and transferred to a Nessler tube.

7. Copper. (1.)

Copper ferrocyanide is produced and the intensity of color of its solution is compared or matched with a standard.

Reagents:

Standard Solution of Copper.—To prepare this, 0.393 Gm. of pure crystalline copper sulphate, $CuSO_4 \cdot 5H_2O$, are carefully weighed and dissolved to measure 1000 Cc. In place of the salt 0.1 Gm. of pure electrolytic copper, dissolved in nitric acid, is evaporated with H_2SO_4 to remove the HNO_3 and the solution diluted to measure 1 Lt.

One (1) Cc. of the solution contains 0.0001 Gm. of copper.

Ammonium Nitrate Solution, 10 per cent.

Potassium Ferrocyanide Solution, 1–25.—Into one Nessler cylinder are placed 5 Cc. of the ferrocyanide solution, then a measured volume of the sample solution is added, the contents diluted to 50 or 100 Cc. and 5 Cc. of the ammonium nitrate solution introduced by means of a pipette. Into the other cylinder the same reagents are measured and the standard copper solution run in from a burette until the color produced in the first is exactly matched. The amount of copper in the sample is then easily calculated.

In canned goods, copper, if present, is found in the solid portion. This should be filtered off, dried on an open filter paper in a petri dish; when dry, it is incinerated, the charred mass digested with HNO_3, diluted with water and filtered, the digestion of the residue in HNO_3 being repeated. The filtrate and washings are evaporated to dryness, the residue taken up with dilute HNO_3, NH_4OH added in excess, the blue solution filtered and the filtrate evaporated to dryness with sulphuric acid. The residue is dissolved in water and treated as above.

Notes.—Ammonium nitrate serves to increase the delicacy of the reaction. The sensitiveness of potassium ferrocyanide is 1–2,500,000. Acids when present modify the color, while bases decompose or dissolve the brown compound formed. Alkaline solutions of copper are acidified with HNO_3 and then neutralized with NH_4OH. Lead in small quantity has no effect; in larger amounts it gives a white precipitate. Lead is readily removed by evaporation with sulphuric

acid. Iron interferes and must be removed. For this purpose the salt is oxidized, if necessary, and the iron precipitated with an excess of ammonium hydroxide. When larger quantities of iron are present, the $Fe(OH)_3$ should be dissolved and reprecipitated, the second filtrate and washings being mixed with the first, and the blue, alkaline liquid neutralized with HNO_3

Very weak solutions should be concentrated by evaporation. Water containing copper is evaporated to dryness, the residue taken up with HNO_3, iron precipitated with NH_4OH and the filtrate treated as above.

Copper may also be determined by comparison of the color produced in its solution by an excess of ammonium hydroxide, with the color of a standard solution similarly treated. This method has been studied by Milbauer and Stanek (Ztsch. anal. Chem., 1907, 46), who found that the indicated copper increases with an increased proportion of NH_4OH and of ammonium carbonate, but decreases with ammonium chloride. Amido acids produce a greenish tint, and give low reading in the same manner as organic compounds and the fixed alkalies.

Comparison of the blue color of copper with the blue of nickel produced by an excess of ammonium hydroxide, has shown that the colors are of the same shade, when, according to Milbauer, the ratio of their concentrations is $Cu = 1 : 18Ni$, in the same complexes.

8. Copper by KCN. (II.)

Reagents:

Standard Solution of $CuSO_4$.—The solution prepared for the ferrocyanide method may be conveniently used.

Solution of KCN.—This should be about 0.1 per cent. and is standardized at the time of the determination; however, for larger quantities of Cu, a nearly 5 per cent. standard solution is used.

Ammonium Hydroxide, 2 per cent.

Measure accurately 10 Cc. of the standard $CuSO_4$ solution into a cylinder of clear, white glass, add the ammonium hydroxide until the precipitate produced is redissolved, dilute to 200 Cc. and titrate with the KCN solution, mixing until the blue color of the solution is just discharged.

Into another cylinder place a definite volume of the solution of sample of known strength, add as much ammonium hydroxide as in the control test, dilute to 200 Cc. and run in the KCN solution carefully until decolorization results.

From the volume of KCN solution consumed calculate the amount of Cu in the sample.

Notes.—Halogens or organic matters must not be present to avoid production of greenish solution. To separate Cu from interfering substances, the Cu is best deposited in metallic form by adding to the solution pure Zn, Cd, or Al. The spongy Cu is filtered off, washed and dissolved in HNO_3, ammonium hydroxide added, and the solution titrated. Small quantities of Pb and Zn do not interfere.

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9. Lead (in Minute Quantities).

Lead sulphide, being the most insoluble lead compound, is formed and the intensity of color compared with that produced by a standard lead solution.

Reagents:

1. *Standard Lead Solution.* — Prepared by dissolving 0.1599 Gm. of pure lead nitrate $Pb(NO_3)_2$ in distilled water to measure 1000 Cc. One (1) Cc. of the solution will contain 0.0001 Gm. of metallic lead.

2. *Solution of Hydrogen Sulphide.* — The saturated solution should be freshly made.

A suitable quantity of the sample, to be treated, is dissolved in distilled water to measure 50 Cc. or, if a sample of potable water, 100 Cc. are measured into a Nessler tube, the solution acidified with 1 Cc. of HCl and 50 Cc. of the hydrogen sulphide solution are added. In another Nessler tube, to an equal volume of water, is added 1 Cc. of the standard lead solution and then the other reagents as to the sample. The contents of the tubes are mixed, the tubes covered, and allowed to stand at 30° to 35° C., during one half hour, when comparison is made. The results will indicate the lead present or the quantity of the standard lead solution that must be used in the following comparison to closely match the color of the sample.

In place of H_2S solution some pass the gas through the contents of Nessler tubes acidified with HNO_3.

The color of the weak solutions depends on the number and size of the PbS particles which are present in colloidal state. Since electrolytes, in solution, tend to coagulate these, they should be absent or the standard test should contain the same proportion of those present in the sample. The reagents employed should be added to both Nessler tubes in the same order. Iron, in small quantities, does not interfere in acid solutions but copper, when present, gives dark color. Copper is made inactive by the addition of just enough KCN solution to destroy the blue color. The solution of sample must be colorless or, if the color is identical with PbS and not intense (yellow KCN color), the allowance to be made for it may be determined with standard lead solution. Organic substances, such as the organic acids, glycerin (especially), sugars, etc., show a marked influence on the development of PbS color. Acetic acid and ammonia show no undesirable effect.

In Citric and Tartaric Acid, lead is determined according to the method of Bennett (Chem. and Drugg., 1904, 633). Of the sample, 10 Gm. are dissolved in 15 Cc. distilled water, 25 Cc. of 10 per cent. NH_4OH added, the solution diluted to 50 Cc. in a Nessler tube and 1 drop of a 10 per cent. Na_2S solution added. In another Nessler tube 50 Cc. of water, containing 1 drop Na_2S solution, are mixed, and the standard lead solution added from a burette until the colors of the two tubes match. Copper, if present, is made passive by the addition of 1 Cc. of 10 per cent. KCN solution. Yellow color of KCN

is corrected, before Na_2S has been added, by standard lead solution in the control test.

10. MANGANESE. (SMALL QUANTITY AS IN IRON AND STEEL.)

Standard Solution of Potassium Permanganate.—This is prepared to contain 0.1438 Gm. of $K_2Mn_2O_8$ in 1000 Cc. by diluting 45.5 Cc. of $\frac{N}{10}$ potassium permanganate V.S. with water, distilled from permanganate, to measure 1000 Cc. 1 Cc. of the standard solution = 0.05 Mgm. of manganese.

Of the sample of iron- or steel-filings, 0.2 Gm. are dissolved in 20 Cc. of nitric acid (1.2 Sp. Gr.) in a 100 Cc. measuring flask by heating to boiling until solution is complete. The liquid is cooled, diluted to 100 Cc., with water, and the contents of the flask mixed by shaking. Ten (10) Cc. of the solution are accurately measured into a beaker, 2 Cc. nitric acid (1.2) added, contents heated to boiling and, after removing flame, 0.5 Gm. of lead dioxide introduced. The mixture is carefully stirred and boiled during 2 minutes. For filtration, ignited asbestos, which has been washed with a solution of permanganate and then with water to remove the latter, is employed. After standing some time the warm solution is filtered through the asbestos into a graduated tube about 20 Cm. high, provided with a glass stopper. The filter is washed with distilled water, until the washings run through, are colorless, the tube is closed and the contents mixed by shaking. Into another graduated tube (duplicate of the first) is introduced 1 Cc. or more of the standard permanganate solution, and water is carefully added to dilute this solution so that the intensity of color should be the same in both tubes when viewed horizontally. From the volume of the standard solution used and the volume to which it is diluted, the quantity of manganese in sample is calculated according to the proportions:

Cc. in tube 1 (stand.) : quant. of Mn in it :: Cc. in tube 2 (sample) : x.

$$0.02 : x :: 100 : x'.$$

$x' =$ per cent. of manganese.

11. BISMUTH. (SMALL QUANTITIES IN P_B, ETC.)

Reagents:

Standard Solution of Bismuth, prepared by dissolving 0.1 Gm. of Bi in HNO_3 and water to make 1 Lt. of solution.
Sulphuric Acid, 1–3.
Potassium Iodide Solution, 20 per cent.

Ten (10) Gm. of a sample are dissolved in HNO_3 (20 Cc. acid and 80 Cc. water), and boiled to remove Sn and Sb. Dilute sulphuric (1.2) is added drop by drop until 60 Cc. have been run in, then 30 Cc. more of 1–3 sulphuric acid are added and the mixture allowed to stand 1 hour. To the liquid is added 5 Cc. of HCl, then a slight excess of ammonium hydroxide and then HCl to just acid

reaction, the mixture boiled 1 minute, filtered, and the filtrate tested for Bi. The precipitate, with the paper, is boiled with 10 Cc. of 1–3 sulphuric acid and 30 Cc. water, cooled, filtered, and the undissolved matter washed with dilute sulphuric acid. The filtrate (if more than 3 Mgm. Bi are present, an aliquot portion of it) is placed in a Nessler tube, 5 Cc. of 20 per cent. KI are added, then 5 Cc. of 1–3 sulphuric acid and 10 drops of sulphurous acid. The coloration produced is matched with the standard bismuth solution, added to the water, and the same reagents used as in the other test.

For bismuth in copper, the sample is dissolved in HNO_3, the solution neutralized with Na_2CO_3 in excess, boiled, and filtered. The precipitate is then treated as above. Ores of Cu, and mattes are dissolved in nitro-hydrochloric acid.

In the presence of As or Sb fusion with Na_2CO_3 and sulphur should precede solution in acid.

12. Gold in Small Quantities. (Method of R. W. Maxson.)

The color of colloidal gold in the sample is matched with a solution of gold of known contents. Weak solution is to be concentrated by evaporation.

A standard solution of gold chloride is employed. As the reagent, a solution of acetylene in water, produced by saturating distilled water with the washed gas, is prepared.

The two tubes, one containing the sample and the acetylene solution, the other only the acetylene, are placed in a dark box and the solutions illuminated from below by a mirror. A sufficient quantity of standard gold chloride solution is added to the control tube to produce the same intensity of color.

Electrolytes in solution interfere, coagulating the gold particles. Their effect may be overcome by the addition of a few drops of ether.

13. Hydrogen Sulphide in Mineral Water.
(Winkler's Method.)

$$Solution\ A = \begin{cases} \text{Rochelle salt, crystals, 25 Gm.} \\ \text{NaOH, 5 Gm.} \\ \text{Lead acetate, 1 Gm.} \\ \text{Water, distilled, to make 1000 Cc.} \end{cases}$$

$$Solution\ B = \begin{cases} \text{Arsenous sulphide } As_2S_3, \text{ 0.0367 Gm.} \\ \text{Ammonium hydroxide, enough to dissolve it.} \\ \text{Water, to make 100 Cc.} \end{cases}$$

As_2S_3 is prepared by dissolving 1 Gm. As_2O_3 in dilute HCl, and adding 100 Cc. of freshly made solution of H_2S; after thorough mixing, filter and dry at 100° C.

1 Cc. of the solution B = 0.1 Cc. of H_2S gas at 0° C. and 760 Mm. For each titration a fresh solution should be made.

Into a flask of 150 Cc. capacity measure 100 Cc. of the sample of water, add 5 Cc. of solution A, and mix well. Compare this color with the coloration produced in another flask containing 100 Cc.

distilled water and 5 Cc. of solution A, by careful addition of solution B, from a burette. The color of the standard should exactly match that of the sample.

Note.—At a spring 100 Cc. bottles are used and are filled to 95 Cc. with the sample, or, with distilled water for a blank. The pipette, by which solution A is introduced, should reach to the bottom of the flask. Sodium thiosulphate has no effect when the volume of H_2S, per liter, is not more than 1.5 Cc.

14. PHOSPHORIC ACID OR PHOSPHATE.

Standard Phosphate Solution, containing 0.5045 Gm. of pure, freshly-crystallized, $Na_2HPO_4 \cdot 12H_2O$ dissolved in water, 100 Cc. of HNO_3 (1.07) added and the solution diluted to measure exactly 1000 Cc. One (1) Cc. = 0.0001 Gm. P_2O_5.

Ammonium Molybdate Solution, 5 per cent.

Comparison is made in tubes, preferably mounted in a suitable camera. Standard tint is prepared from 10 Cc. of standard phosphate solution, diluted to 80, 9 Cc. HNO_3 (1.07), and 8 Cc. ammonium molybdate solution added, and enough water to measure 100 Cc., then allowed to stand 20 minutes. One Cc. of this = 0.00001 Gm. P_2O_5.

Silica interferes, giving yellow color. It may be removed, if present, by dehydration. In place of ammonium molybdate solution, Pouget (Chem. Zeit., 1908, 32, 832) recommends the employment of strychnine molybdate. Solution of this compound must contain 7 to 8 per cent. of nitric acid. Very sensitive with phosphoric acid, 1–12,000,000, the color forming rapidly.

Phosphorus in steel is oxidized, in the HNO_3 solution, with permanganate. The MnO_2 is dissolved in H_2O_2, free from HCl and H_3PO_4 (prepared from $Na_2O_2 + HNO_3$), solution of ammonium vanadate added, and H_2O_2 removed by boiling. To the cooled and diluted solution, ammonium molybdate solution is added and the color produced is compared in 2–3 minutes with that produced with a standard steel solution. The latter is prepared in the same way, and should be renewed weekly. Sensitiveness of 0.005 per cent.

15. SALICYLIC ACID.

Standard Solution of Salicylic Acid.—This is prepared by dissolving 0.1 Gm. of pure salicylic acid in alcohol and diluting with water to measure 1000 Cc. One (1) Cc. of the solution contains 0.0001 Gm. of the acid.

Solution of Ferric Chloride, 0.5 per cent.

The dry acid is weighed and dissolved in alcohol, or a suitable volume of a solution is carefully measured. When present in admixture with other substances, as it is often found in foods or medicinal preparations, 50 Gm. of the sample are extracted with ether, the sample having been previously acidified with sulphuric acid. The extraction is made in a separator, the ethereal extract evaporated, the residue dissolved in hot water or alcohol, filtered,

the filtrate made up to definite volume, and aliquots taken for comparisons.

Into one Nessler tube is placed a definite volume of the sample solution, 1 to 2 Cc. of the ferric chloride added, and diluted with distilled water to measure 50 Cc.; into the other, which should contain an equal volume of ferric chloride and of distilled water, the standard salicylic acid solution is run from a burette and the two tubes are viewed, against a white surface, for comparison. The percentage of salicylic acid in the sample is then calculated from the volume of the standard solution required to produce a color of the same intensity.

In canned tomatoes, catsups, etc., salicylic acid is extracted with ether after the sample has been diluted with water, made alkaline with NaOH solution and milk of lime added; the mixture having been shaken is filtered, the colorless filtrate acidified and extracted.

In the presence of tannin, salicylic acid is precipitated, together with the tannic acid, by basic lead acetate. To the mixture is then added an excess of NaOH in which the salicylate of lead is dissolved, the tannate being insoluble. Harry and Mummery (Analyst, 131, 124) recommend: To 50 Gm. of the pulp of fruit or of jam contained in a 300-Cc. measuring flask are added 15–20 Cc. of a solution of lead subacetate, the mixture made alkaline with 25 Cc. of N–NaOH, a portion of the alkali neutralized with 15–20 Cc. of N–HCl, and the mixture diluted to the mark. After filtration, 200 Cc. of the filtrate are acidified with HCl and extracted with ether. The residue of the ethereal solution is dissolved in alcohol and treated with ferric chloride for color comparison.

Note.—It will be evident that enough ferric chloride must be added to each test to react with all salicylic acid present; however, a large excess of the reagent must be avoided. If the color produced is very intense the mixture should be diluted or, what is to be preferred, a smaller volume of the sample taken for comparison. In the presence of citric and tartaric acids, the color with ferric chloride lacks intensity; the addition of a drop of HNO_3 brings out the color at once.

16. SACCHARIN.   (BENZOYL SULPHINIDE.)

Saccharin is extracted and determined as salicylic acid into which it is first converted. To destroy and remove salicylic acid, naturally existing or added, and also the so-called "false saccharin," the acid solution is extracted with ether and the ether evaporated. The residue, acidified with 2 Cc. of sulphuric acid, 1 : 3, is heated to boiling, and 5 per cent. solution of potassium permanganate added until a permanent pink color is imparted to the solution. The solution, on cooling, is treated with a piece of solid NaOH, the mixture filtered, the filtrate evaporated to dryness in a silver dish or on a silver crucible cover, and the dry mass heated at 210° to 215° C., during 20 minutes. On cooling, this is taken up with water, acidified with HCl, and extracted with ether. The ethereal residue is then dissolved and the solution treated as salicylic acid. (See 15.)

17. FORMALDEHYDE IN MILK.   (A.)   (METHOD OF F. BONNET.[1])

1. *Standard Formaldehyde Solutions.*—Milk containing definite quantities of added formaldehyde (1–10, to 50 thousand).

2. *Solution of Morphine,* 0.35 in 100 Cc. sulphuric acid (1.84).

Of the milk to be tested, 60 Cc. are placed in a 3-inch evaporating dish, and 1 Cc. of the morphine solution floated on its surface in 1-inch water-glass, the dish covered with a glass plate and allowed to stand at 20° C.   Several standard formaldehyde milks are similarly treated.   The coloration produced in the morphine-sulphuric acid, within a definite length of time, is matched with one of the standards, and in that way the quantity of formaldehyde present is ascertained.   Milk containing formaldehyde, 1–25,000, gives distinct color within 1 hour.   Intensity of color depends on the duration of exposure.

Other aldehydes react similarly, but volatile nonaldehydic compounds do not interfere.

Sour milk, containing 1–20,000, gives reaction only if it has been kept in a closed flask.   Butter is treated like milk.

(B.)   (METHOD OF E. W. JONES.[2])

1. *Standard Solution of Formaldehyde.*

2. *Solution of Ferric Chloride in Hydrochloric Acid.*—The solution of this reagent is prepared from 0.25 Gm. of pure iron, converted into ferric chloride, precipitated as ferric hydroxide, the precipitate washed and dissolved in 500 Cc. of concentrated hydrochloric acid.

Ten Cc. of a sample of milk in one test-tube and an equal volume of pure milk (together with 0.1 to 0.2 Cc. standard formaldehyde solution) in two other test-tubes are mixed with 10 Cc. of the reagent, and the tubes heated at 80° to 85° C., during 20 minutes. The contents are then diluted with 30 Cc. of water, cooled, and filtered, the precipitate washed and the filtrate and washings in each case diluted to 100 Cc.   The colors of these solutions are then compared and the formaldehyde present calculated.

18. MORPHINE.

Standard Morphine Solution containing 1 in 1000 Morphine hydrochloride.

Marquis's Reagent.—Mix 3 Cc. concentrated H_2SO_4 with 2 drops of formaldehyde solution, 40 per cent.

One (1) Cc. of the solution of the sample is evaporated to dryness, the residue stirred with 1 Cc. of the reagent and the solution washed into a small tube with 4 Cc. of dilute sulphuric acid.   Of the standard solution 1 Cc. is treated in like manner and the colorations are matched by diluting the more intensely colored liquid with dilute sulphuric acid.   The amount of morphine in the sample is then calculated from the volume of the control solution required to match its color.

[1] J. Am. Ch. Soc., 1906, 27, 601.
[2] Chem. News, 1908, 98, 247.

19. Benzaldehyde.   (Woodman and Lyford.)

Color produced by an aldehyde with fuchsin-SO_2 is proportional in intensity to the amount of the aldehyde, only when the quantity is small.

1. Standard Benzaldehyde Solution.—1–1000 of aldehyde-free wood alcohol.

2. Schiff's Reagent.—Dissolve 0.5 Gm. of pure fuchsine in 100 Cc. of water and add 20 Gm. of SO_2 gas, or a solution containing as much.   The exact quantity of SO_2 present should be determined by titration or found from the Sp. Gr. of the solution.

3. Methyl Alcohol, Free From Aldehyde.—Heat first with a small quantity of Ag_2O, distill, and mix 1000 Cc. of the distillate with 25 Gm. of metaphenylene-diamine hydrochloride and pass a current of air through the mixture during 3 hours.   Keep well stoppered in a cool place.   The alcohol thus treated should give no color with Schiff's reagent.

For determination, a quantity of the sample, containing not more than 5 Mgm. of benzaldehyde is transferred to a tube, 20 Cc. of the accurately measured reagent added and, after mixing, the solution allowed to stand 10 minutes.   Three other tubes containing respectively 2, 4, 6 Mgm. of standard benzaldehyde are treated, each with 20 Cc. of the reagent, and when all four have stood ten minutes, the color of the tube containing the sample is then matched with the nearest color it approaches.   To make the comparison exact, some of the stronger-colored standard should be removed by a pipette until equally matched.

The method may be applied to other aldehydes.

20. Furfural.   (In Whiskey or Brandy.)

1. Standard Solution of Furfural = 0.001 per cent. to 0.0005 per cent. of pure furfural.

2. Aniline Acetate Solution.—Prepared by boiling equal volumes of freshly distilled aniline, glacial acetic acid and water, during 3 minutes.

In a small cylinder (a test-tube with flattened bottom) are placed 5 Cc. of the sample, water to measure 19 Cc. is added, and 1 Cc. of the aniline acetate introduced.

In another tube a small volume of the standard solution is treated with the same reagent in like manner and after mixing the tubes are allowed to stand 15 minutes.

The solutions are then compared as to color within the same period of time.

TABLE OF MULTIPLES OF ATOMIC OR MOLECULAR WEIGHTS OF IMPORTANT
ELEMENTS AND GROUPS OF SUCH.

	1	2	3	4	5	6	7	8	9
H	1.01	2.02	3.03	4.04	5.05	6.06	7.07	8.08	9.09
O	16	32	48	64	80	96	112	128	144
OH	17.01	34.02	51.03	68.04	85.05	102.06	119.07	136.08	153.09
H_2O	18.02	36.04	54.06	72.08	90.10	108.12	126.14	144.16	162.18
N	14 01	28.02	42.03	56.04	70.05	84.06	98.07	112.08	126.09
NH_2	16.03	32.06	48.09	64.12	80.15	96.18	112.21	128.24	144.27
NH_3	17.04	34.08	51.12	68.16	85.20	102.24	119.28	136.32	153.36
NH_4	18.05	36.10	54.15	72.20	90.25	108.30	126.35	144.40	162.45
NO_2	46.01	92.02	138.03	184.04	230.05	276.06	312.07	388.08	414.09
NO_3	62.01	124.02	186.03	248.04	310.05	372.06	434.07	496.08	558.09
C	12	24	36	48	60	72	84	96	108
CO_2	44	88	132	176	220	264	308	352	396
CO_3	60	120	180	240	300	360	420	480	540
CN	26.01	52.02	78.03	140.04	130.05	156.06	182.07	208.08	234.09
Cl	35.46	70.92	106.38	141.84	177.30	212.76	248.22	283.68	319.14
Br	79.92	159.84	239.76	319.68	399.60	479.52	559.44	639.36	719.28
I	126.92	253.84	380.76	507.68	634.60	761.52	888.44	1015.36	1142.28
S	32.07	64.14	96.21	128.28	160.35	192.42	224.49	256.56	288.63
SO_2	64.07	128.14	192.21	256.28	320.35	384.42	448.49	512.56	576.63
SO_3	80.07	160.14	240.21	320.28	400.35	480.42	560.49	640.56	720.63
SO_4	96.07	192.14	288.21	384.28	480.35	586.42	672.49	768.56	864.63
PO_4	95	190	285	380	475	570	665	760	855
P_2O_5	142	284	426	568	710	852	994	1136	1278
Na	23	46	69	92	115	138	161	184	207
K	39.1	78.20	117.30	156.40	195.50	234.60	273.70	312.80	351.90

APPENDIX.

TABLE OF ATOMIC WEIGHTS.[1]

Basis : $O = 16$.

Aluminium	Al	27.1
Antimony	Sb	120.2
Arsenic	As	75.
Barium	Ba	137.37
Bismuth	Bi	208.
Boron	B	11.
Bromine	Br	79.92
Cadmium	Cd	112.4
Calcium	Ca	40.09
Carbon	C	12.
Chlorine	Cl	35.46
Chromium	Cr	52.1
Cobalt	Co	58.97
Copper	Cu	63.57
Fluorine	F	19.
Gold	Au	197.2
Hydrogen	H	1.008
Iodine	I	126.92
Iron	Fe	55.85
Lead	Pb	207.1
Lithium	Li	7.
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury	Hg	200.
Molybdenum	Mo	96.
Nickel	Ni	58.68
Nitrogen	N	14.01
Oxygen	O	16.
Phosphorus	P	31.
Platinum	Pt	195.
Potassium	K	39.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver	Ag	107.88
Sodium	Na	23.
Strontium	Sr	87.62
Sulphur	S	32.07
Tin	Sn	119.
Uranium	U	238.5
Zinc	Zn	65.7

[1] International Atomic Weights, 1909.

LIST OF THE CHEMICAL ELEMENTS AND COMPOUNDS OF IMPORTANCE IN VOLUMETRIC ANALYSIS.

ATOMIC OR MOLECULAR WEIGHTS.

Basis : $O = 16$.

Acetone	$(CH_3)_2CO,$	58.06
Acid, Acetic	$HC_2H_3O_2,$	60.04
" Arsenous	$As_2O_3,$	198.
" Benzoic	$HC_7H_5O_2,$	122.06
" Boric	$H_3BO_3,$	62.03
" Carbolic. (See Phenol.)		
" Carbonic (anhydride)	$CO_2,$	44.
" Chromic	$CrO_3,$	100.1
" Citric	$H_3C_6H_5O_7 + H_2O,$	210.1
" Citric, anhydrous	$H_3C_6H_5O_7,$	192.08
" Formic	$HCO_2H,$	46.02
" Gallic	$HC_7H_5O_5 + H_2O,$	188.08
" Gallic, anhydrous	$HC_7H_5O_5,$	170.06
" Hydriodic	$HI,$	127.93
" Hydrobromic	$HBr,$	80.93
" Hydrochloric	$HCl,$	36.47
" Hydrocyanic	$HCN,$	27.02
" Hydrofluoric	$HF,$	20.01
" Hydrofluosilicic	$H_2SiFl_6,$	144.32
" Hydrosulphuric. (See Hydrogen Sulphide).		
" Hypophosphorous	$HPH_2O_2,$	66.03
" Lactic	$HC_3H_5O_3,$	90.06
" Molybdic	$H_2MoO_4,$	162.02
" Nitric	$HNO_3,$	63.02
" Oleic	$HC_{18}H_{33}O_2,$	282.34
" Oxalic	$H_2C_2O_4 + 2H_2O,$	126.06
" Oxalic, anhydrous	$H_2C_2O_4,$	90.02
" Phosphoric	$H_3PO_4,$	98.03
" Phosphorous	$H_3PO_3,$	82.03
" Salicylic	$HC_7H_5O_3,$	138.06
" Stearic	$HC_{18}H_{35}O_2,$	284.32
" Succinic	$H_2C_4H_4O_4,$	118.06
" Sulphanilic	$HC_6H_4(NH_2)SO_3 + 3H_2O,$	227.21
" Sulphanilic, anhydrous	$HC_6H_4(NH_2)SO_3,$	173.15
" Sulphuric	$H_2SO_4,$	98.09
" Sulphurous	$H_2SO_3,$	82.09
" Tannic	$HC_{14}H_9O_9,$	322.10
" Tartaric	$H_2C_4H_4O_6,$	150.06
" Trichloracetic	$HC_2Cl_3O_2,$	163.39
Aconitine	$C_{34}H_{47}NO_{11},$	645.48
Alcohol, Ethylic	$C_2H_5OH,$	46.06
Alcohol, methylic	$CH_3OH,$	32.04
Alum (Potassium)	$AlK(SO_4)_2 + 12H_2O,$	474.58
Alum (Potassium), anhydrous	$AlK(SO_4)_2,$	258.34
Aluminium	**Al,**	27.10

Ammonia	NH_3,	17.04
Ammonium Acetate	$NH_4C_2H_3O_2$,	77.08
" Benzoate	$NH_4C_7H_5O_2$,	139.10
" Bromide	NH_4Br,	97.97
" Carbonate (Normal)	$(NH_4)_2CO_3$,	96.10
" Carbonate (U. S. P.)	$NH_4HCO_3 \cdot NH_4NH_2CO_2$,	157.14
" Chloride	NH_4Cl,	53.51
" Citrate	$(NH_4)_3C_6H_5O_7$,	243.20
" Iodide	NH_4I,	144.97
" Lactate	$NH_4C_3H_5O_3$,	107.10
" Magnesium Phosphate	NH_4MgPO_4,	137.37
" Molybdate	$(NH_4)_6Mo_7O_{24} + 4H_2O$,	1236.38
" Nitrate	NH_4NO_3,	80.06
" Oxalate	$(NH_4)_2C_2O_4 + H_2O$,	142.15
" Oxalate, anhydrous	$(NH_4)_2C_2O_4$,	124.10
" Persulphate	$(NH_4)_2S_2O_8$,	228.24
" Salicylate	$NH_4C_7H_5O_3$,	155.10
" Sulphate	$(NH_4)_2SO_4$,	132.17
" and Sodium Phosphate	$NH_4NaHPO_4 + 4H_2O$,	209.14
" Sulphide	$(NH_4)_2S$,	68.17
" Tartrate	$(NH_4)_2C_4H_4O_6$,	184.14
" Thiocyanate	NH_4SCN,	76.13
" Triiodate	$(NH_4)H_2(IO_3)_3$,	544.83
Antimony	**Sb,**	120.20
Antimony Oxide (Trioxide)	Sb_2O_3,	288.40
" and Potassium Tartrate	$2K(SbO)C_4H_4O_6 + H_2O$,	664.70
" and Potassium Tartrate, anhydrous,	$K(SbO)C_4H_4O_6$,	323.34
" Tri-Sulphide	Sb_2S_3,	336.61
" Penta-Sulphide	Sb_2S_5,	400.75
Apomorphine Hydrochloride	$C_{17}H_{17}NO_2HCl$,	303.65
Arsenic	**As,**	75.00
Arsenic Iodide	AsI_3,	455.76
" Tri-Sulphide	As_2S_3,	246.21
" Trioxide. (See Acid, Arsenous.)		
" Penta-Sulphide	As_2S_5,	310.35
Atropine	$C_{17}H_{23}NO_3$,	289.24
Atropine, Sulphate	$(C_{17}H_{23}NO_3)_2H_2SO_4$,	676.57
Barium	**Ba,**	137.37
Barium Carbonate	$BaCO_3$,	197.37
" Chloride	$BaCl_2 + 2H_2O$,	244.33
" Chloride, anhydrous	$BaCl_2$,	208.29
" Chromate	$BaCrO_4$,	253.47
" Dioxide	BaO_2,	169.37
" Hydroxide	$Ba(OH)_2 + 8H_2O$,	315.55
" Hydroxide, anhydrous	$Ba(OH)_2$	171.39
" Nitrate	$Ba(NO_3)_2$,	261.39
" Sulphate	$BaSO_4$,	233.44
" Sulphide	BaS,	169.44
Berberine	$C_{20}H_{17}NO_4$,	335.28
Benzoyl Sulphinide (Saccharin)	$C_7H_5NSO_3$,	183.13
Benzaldehyde	C_7H_6O,	106.06
Bismuth	**Bi,**	208.
Bismuth Citrate	$BiC_6H_5O_7$,	397.05
" Nitrate (Normal)	$Bi(NO_3)_3 + 5H_2O$,	484.13
" Salicylate	$Bi(OH)_2C_7H_5O_3$,	379.07
" Sulphide	Bi_2S_3,	512.21
" Trioxide	Bi_2O_3,	464.
Boron	**B,**	11.
Boron Trioxide	B_2O_3,	70.
Bromine	**Br,**	79.92
Bromoform	$CHBr_3$,	252.77
Brucine	$C_{23}H_{26}N_2O_4 + 4H_2O$,	466.36
Brucine, anhydrous	$C_{23}H_{26}N_2O_4$,	394.28

Cadmium	**Cd,**	112.40
Cadmium Sulphate	$3CdSO_4 + 8H_2O,$	769.57
Cadmium Sulphide	$CdS,$	144.47
Cæsium	**Cs,**	132.81
Caffeine	$C_8H_{10}N_4O_2 + H_2O,$	212.16
Caffeine, anhydrous	$C_8H_{10}N_4O_2,$	194.14
Calcium	**Ca,**	40.09
Calcium Bromide	$CaBr_2,$	199.93
" Carbonate	$CaCO_3,$	100.09
" Chloride	$CaCl_2 + 6H_2O,$	219.13
" Chloride, anhydrous	$CaCl_2,$	111.01
" Fluoride	$CaF_2,$	78.09
" Hydroxide	$Ca(OH)_2,$	74.11
" Hypophosphite	$Ca(PH_2O_2)_2,$	170.13
" Oxalate	$CaC_2O_4 + 2H_2O,$	164.13
" Oxide	$CaO,$	56.09
" Phosphate	$Ca_3(PO_4)_2,$	310.27
" Sulphate (Gypsum)	$CaSO_4 + 2H_2O,$	172.20
" Sulphate, anhydrous	$CaSO_4,$	136.16
" Sulphide (Monosulphide) ...	$CaS,$	72.16
Carbon	**C,**	12.
Carbon Disulphide	$CS_2,$	76.14
Carbon Tetrachloride	$CCl_4,$	153.94
Cephaëline	$C_{14}H_{19}NO_2,$	233.20
Cerium	**Ce,**	140.25
Cerium Oxalate	$Ce_2(C_2O_4)_3 + 10H_2O,$	724.70
Cerium Oxalate, anhydrous	$Ce_2(C_2O_4)_3,$	544.50
Chloral, anhydrous	$C_2HCl_3O,$	147.39
Chloral Hydrate	$C_2HCl_3O + H_2O,$	165.41
Chlorine	**Cl,**	35.46
Chloroform	$CHCl_3,$	119.39
Chromium	**Cr,**	52.10
Chromium Oxide	$Cr_2O_3,$	152.20
Cinchonidine	$C_{19}H_{22}N_2O,$	294.24
Cinchonidine Salicylate	$C_{19}H_{22}N_2OC_7H_6O_3,$	432.30
Cinchonidine Sulphate	$(C_{19}H_{22}N_2O)_2H_2SO_4 + 3H_2O,$	740.63
Cinchonidine Sulphate, anhydrous	$(C_{19}H_{22}N_2O)_2H_2SO_4,$	686.57
Cinchonine	$C_{19}H_{22}N_2O,$	294.24
Cinchonine, Sulphate	$(C_{19}H_{22}N_2O)_2H_2SO + 2H_2O,$	722.61
Cinchonine, Sulphate, anhydrous	$(C_{19}H_{22}N_2O)_2H_2SO_4,$	686.57
Cobalt	**Co,**	58.97
Cocaine	$C_{17}H_{21}NO_4,$	303.22
Cocaine Hydrochloride	$C_{17}H_{21}NO_4HCl,$	339.69
Codeine	$C_{18}H_{21}NO_3 + H_2O,$	317.24
" anhydrous	$C_{18}H_{21}NO_3,$	299.22
" Phosphate	$C_{18}H_{21}NO_3H_3PO_4 + 2H_2O,$	433.29
" Phosphate, anhydrous	$C_{18}H_{21}NO_3H_3PO_4,$	397.25
" Sulphate	$(C_{18}H_{21}NO_3)_2H_2SO_4 + 5H_2O,$	786.63
" Sulphate, anhydrous	$(C_{18}H_{21}NO_3)_2H_2SO_4,$	696.53
Colchicine	$C_{22}H_{25}NO_6,$	399.26
Coniine	$C_8H_{17}N,$	127.18
Copper	**Cu,**	63.57
Cupric Ammonium Sulphate	$Cu(NH_3)_4SO_4 + H_2O,$	245.82
" Sulphate	$CuSO_4 + 5H_2O,$	249.74
" Sulphate, anhydrous	$CuSO_4,$	159.64
" Sulphide	$CuS,$	95.64
" Tartrate	$CuC_4H_4O_6 + 3H_2O,$	265.67
Cuprous Thiocyanate	$CuSCN,$	121.65
Daturine	$C_{17}H_{23}NO_3,$	289.24
Emetine	$C_{15}H_{21}NO_2,$	247.22
Ferric Acetate	$Fe(C_2H_3O_2)_3,$	232.94
" Ammonium Sulphate	$Fe(NH_4)(SO_4)_2 + 12H_2O,$	482.28
" Ammo. Sulphate, anhydrous ..	$Fe(NH_4)(SO_4)_2,$	266.04
" Chloride	$FeCl_3 + 6H_2O,$	270.35

Ferric Chloride, anhydrous	$FeCl_3$,	162.23
" Hydroxide	$Fe(OH)_3$,	106.88
" Hypophosphite	$Fe(PH_2O_2)_3$,	250.91
" Nitrate	$Fe(NO_8)_3$,	241.88
" Oxide	Fe_2O_3,	159.70
" Phosphate	$FePO_4$,	150.85
" Sulphate (Tersulphate)	$Fe_2(SO_4)_3$,	399.91
Ferrous Bromide	$FeBr_2$,	215.69
" Carbonate	$FeCO_3$,	115.85
" Chloride	$FeCl_2$,	126.77
" Iodide	FeI_2,	309.69
" Lactate	$Fe(C_3H_5O_3)_2 + 3H_2O$,	288.01
" Sulphate	$FeSO_4 + 7H_2O$,	278.06
" Sulphate, anhydrous	$FeSO_4$,	151.92
" Sulphide	FeS,	87.92
Fluorine	**F,**	19.
Formaldehyde	H_2CO,	30.02
Glucose. (See Sugar, Grape.)		
Glycerin	$C_3H_5(OH)_3$,	92.08
Gold	**Au,**	197.20
Gold Chloride	$AuCl_3$,	303.58
Heroine Hydrochloride	$C_{17}H_{17}(C_2H_3O_2)_2NOHCl$,	405.71
Homatropine Hydrobromide	$C_{16}H_{21}NO_3HBr$,	356.15
Hydrastine	$C_{21}H_{21}NO_6$	383.22
Hydrastine Hydrochloride	$C_{21}H_{21}NO_6HCl$,	419.69
Hydrastinine Hydrochloride	$C_{11}H_{11}NO_2HCl$,	225.59
Hydrogen	**H,**	1.008
Hydrogen Dioxide	H_2O_2,	34.02
Hydrogen Sulphide	H_2S,	34.09
Hyoscine Hydrobromide	$C_{17}H_{21}NO_4HBr + 3H_2O$,	438.21
Hyoscine Hydrobromide, anhydrous	$C_{17}H_{21}NO_4HBr$,	384.15
Hyoscyamine	$C_{17}H_{23}NO_3$,	289.24
Hyoscyamine Hydrobromide	$C_{17}H_{23}NO_3HBr$,	370.17
Hyoscyamine Sulphate	$(C_{17}H_{23}NO_8)_2H_2SO_4$,	676.57
Iodine	**I,**	126.92
Iodoform	CHI_3,	393.77
Iodol	C_4I_4NH,	570.70
Iron	**Fe,**	55.85
Iron Salts. See under *Ferric* and *Ferrous*.		
Lead	**Pb,**	207.10
Lead Acetate	$Pb(C_2H_3O_2)_2 + 3H_2O$,	379.22
" Acetate, anhydrous	$Pb(C_2H_3O_2)_2$,	325.16
" Carbonate	$(PbCO_3)_2Pb(OH)_2$,	775.32
" Chloride	$PbCl_2$,	278.02
" Chromate	$PbCrO_4$,	323.20
" Iodide	PbI_2,	460.94
" Nitrate	$Pb(NO_3)_2$,	331.12
" Oxide	PbO,	223.10
" Subacetate (approximately)	$Pb_2O(C_2H_3O_2)_2$,	548.26
" Sulphate	$PbSO_4$,	303.17
" Sulphide	PbS,	239.17
Lime. (See Calcium Oxide.)		
Lithium	**Li,**	7.
Lithium Benzoate	$LiC_7H_5O_2$,	128.05
" Bromide	$LiBr$,	86.92
" Carbonate	Li_2CO_3,	74.
" Citrate	$Li_3C_6H_5O_7 + 4H_2O$,	282.13
" Salicylate	$LiC_7H_5O_3$,	144.05
" Sulphate, anhydrous	Li_2SO_4,	110.07
Magnesia. (See Magnesium Oxide.)		
Magnesium	**Mg,**	24.32
Magnesium Carbonate (approximately)	$(MgCO_3)_4Mg(OH)_2 + 5H_2O$,	485.72
" Oxide	MgO,	40.32
" Sulphate	$MgSO_4 + 7H_2O$,	246.53

Magnesium Sulphate, anhydrous	$MgSO_4$,	120.39
Manganese	**Mn,**	54.93
Manganese Dioxide	MnO_2,	86.93
Manganese Hypophosphite	$Mn(PH_2O_2)_2 + H_2O$,	202.99
Manganous Sulphate	$MnSO_4 + 4H_2O$,	223.08
Manganous Sulphate, anhydrous	$MnSO_4$,	151.00
Mercuric-Ammonium Chloride	$HgClNH_2$,	251.49
" Chloride	$HgCl_2$,	270.92
" Cyanide	$Hg(CN)_2$,	252.02
" Iodide	HgI_2,	453.84
" Nitrate	$Hg(NO_3)_2 + 4H_2O$,	396.10
" Nitrate, anhydrous	$Hg(NO_3)_2$,	324.02
" Oxide	HgO,	216.
" Potassium Iodide	$HgI_2 + 2KI$,	785.88
" Subsulphate	$Hg(HgO)_2SO_4$,	728.07
" Sulphate	$HgSO_4$,	296.07
" Sulphide	HgS,	232.07
Mercurous Chloride	Hg_2Cl_2,	470.92
" Iodide	Hg_2I_2,	653.84
" Nitrate	$Hg_2(NO_3)_2 + H_2O$,	542.04
" Sulphate	Hg_2SO_4,	496.07
Mercury	**Hg,**	200.
Methyl Orange	$NaC_{14}H_{14}N_3SO_3$,	327.24
Molybdenum	**Mo,**	96.
Morphine	$C_{17}H_{19}NO_8 + H_2O$,	303.22
" anhydrous	$C_{17}H_{19}NO_3$,	285.20
" Acetate (variable)	$C_{17}H_{19}NO_3C_2H_4O_2 + 3H_2O$,	399.30
" Hydrochloride	$C_{17}H_{19}NO_3HCl + 3H_2O$,	375.73
" Hydrochloride, anhydrous	$C_{17}H_{19}NO_3HCl$,	321.67
" Sulphate	$(C_{17}H_{19}NO_3)_2H_2SO_4 + 5H_2O$,	758.59
" Sulphate, anhydrous	$(C_{17}H_{19}NO_3)_2H_2SO_4$,	668.49
Nickel	**Ni,**	58.68
Nickelous Oxide	NiO,	74.68
Nickelous Sulphate	$NiSO_4 + 7H_2O$,	280.89
Nitrogen	**N,**	14.01
Oxygen	**O,**	16.
Phenol. (Acid, Carbolic.)	C_6H_6O,	94.06
Phenolphthalein	$C_{20}H_{14}O_4$,	318.14
Phosphorus	**P,**	31.
Physostigmine	$C_{15}H_{21}N_3O_2$,	275.24
Physostigmine Salicylate	$C_{15}H_{21}N_3O_2C_7H_6O_3$,	413.30
Physostigmine Sulphate	$(C_{15}H_{21}N_3O_2)_2H_2SO_4$,	648.57
Picrotoxin	$C_{30}H_{34}O_{13}$,	602.34
Pilocarpine	$C_{11}H_{16}N_2O_2$,	208.18
Pilocarpine Hydrochloride	$C_{11}H_{16}N_2O_2HCl$,	244.65
Pilocarpine Nitrate	$C_{11}H_{16}N_2O_2HNO_3$,	271.20
Platinic Chloride (in solution)	$PtCl_4$,	336.84
Platinum	**Pt,**	195.
Potassa. (See Potassium Hydroxide.)		
Potassium	**K,**	39.10
Potassium Acetate	$KC_2H_3O_2$,	98.13
" Arsenite (Metarsinite)	$KAsO_2$,	146.10
" Benzoate	$KC_7H_5O_2 + 3H_2O$,	214.21
" Benzoate, anhydrous	$KC_7H_5O_2$,	160.15
" Bicarbonate	$KHCO_3$,	100.11
" Bichromate. (See Dichromate.)		
" Bisulphate	$KHSO_4$,	136.18
" Bitartrate	$KHC_4H_4O_6$,	188.15
" Bromate	$KBrO_3$,	167.02
" Bromide	KBr,	119.02
" Carbonate	K_2CO_3,	138.20
" Chlorate	$KClO_3$,	122.56
" Chloride	KCl,	74.56
" Chromate	K_2CrO_4,	194.30

Potassium	Citrate	$K_3C_6H_5O_7 + H_2O$,	324.37
"	Citrate, anhydrous	$K_3C_6H_5O_7$,	306.35
"	Cyanide	KCN,	65.11
"	Dichromate	$K_2Cr_2O_7$,	294.40
"	Diiodate	$KH(IO_3)_2$,	389.95
"	Ferricyanide	$K_3Fe(CN)_6$,	329.21
"	Ferrocyanide	$K_4Fe(CN)_6 + 3H_2O$,	422.37
"	Ferrocyanide, anhydrous ..	$K_4Fe(CN)_6$,	368.31
"	Hydroxide	KOH,	56.11
"	Hypophosphite	KPH_2O_2,	104.12
"	Iodate	KIO_3,	214.02
"	Iodide	KI,	166.02
"	Lactate	$KC_3H_5O_3$,	128.15
"	Nitrate	KNO_3,	101.11
"	Permanganate	$K_2Mn_2O_8$,	316.06
"	Percarbonate	$K_2C_2O_6 + H_2O$,	216.22
"	Persulphate	$K_2S_2O_8$,	270.34
"	Phosphate	K_2HPO_4,	174.21
"	Salicylate	$KC_7H_5O_3$,	176.15
"	and Sodium Tartrate	$KNaC_4H_4O_6 + 4H_2O$,	282.22
"	and Sodium Tartrate, anhydrous,	$KNaC_4H_4O_6$,	210.14
"	Sulphate	K_2SO_4,	174.27
"	Sulphite	$K_2SO_3 + 2H_2O$,	194.37
"	Sulphite, anhydrous	K_2SO_3,	158.27
"	Thiocyanate	KSCN,	97.18
"	Tartrate	$2K_2C_4H_4O_6 + H_2O$,	470.50
"	Tartrate, anhydrous	$K_2C_4H_4O_6$,	226.24
Pyrogallol		$C_6H_6O_3$,	126.06
Quinidine Sulphate		$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 2H_2O$,	782.65
Quinidine Sulphate, anhydrous		$(C_{20}H_{24}N_2O_2)_2H_2SO_4$,	746.61
Quinine		$C_{20}H_{24}N_2O_2 + 3H_2O$,	378.32
"	anhydrous	$C_{20}H_{24}N_2O_2$,	324.26
"	Bisulphate	$C_{20}H_{24}N_2O_2H_2SO_4 + 7H_2O$,	548.49
"	Bisulphate, anhydrous	$C_{20}H_{24}N_2O_2H_2SO_4$,	422.35
"	Hydrobromide	$C_{20}H_{24}N_2O_2HBr + H_2O$,	423.21
"	Hydrobromide, anhydrous ...	$C_{20}H_{24}N_2O_2HBr$,	405.19
"	Hydrochloride	$C_{20}H_{24}N_2O_2HCl + 2H_2O$,	396.77
"	Hydrochloride, anhydrous ...	$C_{20}H_{24}N_2O_2HCl$,	360.73
"	Salicylate	$2C_{20}H_{24}N_2O_2C_7H_6O_3 + H_2O$,	942.66
"	Sulphate	$(C_{20}H_{24}N_2O_2)_2H_2SO_4 + 7H_2O$,	872.75
"	Sulphate, anhydrous	$(C_{20}H_{24}N_2O_2)_2H_2SO_4$,	746.61
"	Valerianate (Valerate)	$C_{20}H_{24}N_2O_2C_5H_{10}O_2 + H_2O$,	444.40
Resorcinol (Resorcin)		$C_6H_6O_2$,	110.06
Scopolamine Hydrobromide		$C_{17}H_{21}NO_4HBr + 3H_2O$,	438.21
Scopolamine Hydrobromide, anhydrous		$C_{17}H_{21}NO_4HBr$,	384.15
Selenium		**Se**,	78.60
Silicon		**Si**,	28.30
Silicon Oxide (Silica)		SiO_2,	60.30
Silver		**Ag**,	107.88
Silver Chloride		AgCl,	143.34
"	Cyanide	AgCN,	133.89
"	Iodide	AgI,	234.80
"	Nitrate	$AgNO_3$,	169.89
"	Oxide	Ag_2O,	231.76
"	Sulphate	Ag_2SO_4,	311.83
"	Sulphide	Ag_2S,	247.83
Soda. (See Sodium Hydroxide.)			
Sodium		**Na**,	23.
Sodium Acetate		$NaC_2H_3O_2 + 3H_2O$,	136.09
"	Acetate, anhydrous	$NaC_2H_3O_2$,	82.03
"	Arsenate	$Na_2HAsO_4 + 7H_2O$,	312.15
"	Arsenate, anhydrous	Na_2HAsO_4,	186.01
"	Arsenite (Metarsenite)	$NaAsO_2$,	130.

Sodium	Benzoate	$NaC_7H_5O_2$,	144.05
"	Bicarbonate	$NaHCO_3$,	84.01
"	Bisulphite	$NaHSO_3$,	104.08
"	Bitartrate	$NaHC_4H_4O_6 + H_2O$,	190.07
"	Borate	$Na_2B_4O_7 + 10H_2O$,	382.20
"	Borate, anhydrous	$Na_2B_4O_7$,	202.
"	Bromate	$NaBrO_3$,	150.92
"	Bromide	$NaBr$,	102.92
"	Carbonate	$Na_2CO_3 + 10H_2O$,	286.20
"	Carbonate, anhydrous	Na_2CO_3,	106.
"	Carbonate, monohydrated	$Na_2CO_3 + H_2O$,	124.02
"	Chlorate	$NaClO_3$,	106.46
"	Chloride	$NaCl$,	58.46
"	Citrate	$2Na_3C_6H_5O_7 + 11H_2O$,	714.32
"	Citrate, anhydrous	$Na_3C_6H_5O_7$,	258.05
"	Cobaltic nitrite	$Co_2(NO_2)_6 6NaNO_2 + H_2O$,	826.08
"	Dioxide	Na_2O_2,	78.
"	Hydroxide	$NaOH$,	40.01
"	Hypophosphite	$NaPH_2O_2 + H_2O$,	106.04
"	Hyposulphite. (See Thiosulphate.)		
"	Iodide	NaI,	149.92
"	Lactate	$NaC_3H_5O_3$,	112.05
"	Nitrate	$NaNO_3$,	85.01
"	Nitrite	$NaNO_2$,	69.01
"	Nitroprusside	$Na_2Fe(NO)(CN)_5 + 2H_2O$,	297.95
"	Perborate	$NaBO_3 + 4H_2O$,	154.10
"	Persulphate	$Na_2S_2O_8$,	238.14
"	Phosphate	$Na_2HPO_4 + 12H_2O$,	358.25
"	Phosphate, anhydrous	Na_2HPO_4,	142.01
"	Pyrophosphate	$Na_4P_2O_7 + 10H_2O$,	446.20
"	Pyrophosphate, anhydrous	$Na_4P_2O_7$,	266.
"	Salicylate	$NaC_7H_5O_3$,	160.05
"	Sulphate	$Na_2SO_4 + 10H_2O$,	322.27
"	Sulphate, anhydrous	Na_2SO_4,	142.07
"	Sulphite	$Na_2SO_3 + 7H_2O$,	252.21
"	Sulphite, anhydrous	Na_2SO_3,	126.07
"	Tartrate	$Na_2C_4H_4O_6 + 2H_2O$,	230.08
"	Thiosulphate	$Na_2S_2O_3 + 5H_2O$,	248.24
"	Thiosulphate, anhydrous	$Na_2S_2O_3$,	158.14
Sparteine		$C_{15}H_{26}N_2$,	234.28
Sparteine Sulphate		$C_{15}H_{26}N_2H_2SO_4 + 4H_2O$,	404.45
Sparteine Sulphate, anhydrous		$C_{15}H_{26}N_2H_2SO_4$,	332.37
Stannic Chloride		$SnCl_4$,	260.84
Stannous Chloride		$SnCl_2 + 2H_2O$,	225.96
Strontium		**Sr,**	87.62
Strontium	Bromide	$SrBr_2 + 6H_2O$,	355.58
"	Bromide, anhydrous	$SrBr_2$,	247.46
"	Carbonate	$SrCO_3$,	147.62
"	Iodide	$SrI_2 + 6H_2O$,	449.58
"	Iodide, anhydrous	SrI_2,	341.46
"	Lactate	$Sr(C_3H_5O_3)_2 + 3H_2O$,	319.78
"	Lactate, anhydrous	$Sr(C_3H_5O_3)_2$,	265.72
"	Salicylate	$Sr(C_7H_5O_3)_2 + 2H_2O$,	397.76
"	Sulphate	$SrSO_4$,	183.69
Strychnine		$C_{21}H_{22}N_2O_2$,	334.24
"	Nitrate	$C_{21}H_{22}N_2O_2HNO_3$,	397.26
"	Sulphate	$(C_{21}H_{22}N_2O_2)_2H_2SO_4 + 5H_2O$,	856.67
"	Sulphate, anhydrous	$(C_{21}H_{22}N_2O_2)_2H_2SO_4$,	766.57
Sugar, Cane		$C_{12}H_{22}O_{11}$,	342.22
Sugar, Grape		$C_6H_{12}O_6$,	180.12
Sugar, Malt		$C_{12}H_{22}O_{11}$,	342.22
Sugar, Milk		$C_{12}H_{22}O_{11} + H_2O$,	360.24
Sulphur		**S,**	32.07
Sulphur Dioxide		SO_2,	64.07

Tellurium .... **Te,**		127.50
Tin .... **Sn,**		119.
Tin-Salts. (See under *Stannic* and *Stannous.*)		
Uranium .... **U,**		238.50
Uranium Acetate .... $UO_2(C_2H_3O_2)_2 + 2H_2O,$		424.60
Water .... $H_2O,$		18.02
Zinc .... **Zn,**		65.70
Zinc Acetate .... $Zn(C_2H_3O_2)_2 + 2H_2O,$		219.80
" Acetate, anhydrous .... $Zn(C_2H_3O_2)_2,$		183.76
" Bromide .... $ZnBr_2,$		225.54
" Carbonate (normal, not U.S.P.) . $ZnCO_3,$		125.70
" Chloride .... $ZnCl_2,$		136.62
" Iodide .... $ZnI_2,$		319.54
" Oxide .... $ZnO,$		81.70
" Phosphide .... $Zn_3P_2,$		259.10
" Sulphate .... $ZnSO_4 + 7H_2O,$		287.91
" Sulphate, anhydrous .... $ZnSO_4,$		161.77
" Sulphide .... $ZnS,$		97.77
" Sulphocarbolate .. .. $Zn(C_6H_4(OH)SO_3)_2 + 8H_2O,$		556.10
" Valerianate (Valerate) .... $Zn(C_5H_9O_2)_2 + 2H_2O,$		303.92

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